

AD-A100 525

AEROCHEM RESEARCH LABS INC PRINCETON NJ
CORRELATION OF SOOT FORMATION IN TURBOJET ENGINES AND IN LABORATORY--ETC(U)
FEB 81 R K GOULD, D B OLSON, H F CALCOTE
AEROCHEM-TP-407

F/G 21/4

F49620-77-C-0029

AFESC/ESL-TR-81-09

NL

UNCLASSIFIED

1 OF 1
AD-A100 525

END

DATE

TIME

7-8h

OTIC

AD A100525

CORRELATION OF SOOT FORMATION IN TURBOJET ENGINES AND IN LABORATORY FLAMES

R. K. GOULD
D. B. OLSON
H. F. CALCOTE

LEVEL II

AEROCHEM RESEARCH LABORATORIES, INC.
P.O. BOX 12
PRINCETON, NJ 08540

FEBRUARY 1981
FINAL REPORT
AUGUST 1980 — SEPTEMBER 1980

DTIC
SELECTED
S JUN 23 1981 D

E

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

DTIC FILE COPY



ENGINEERING & SERVICES LABORATORY
AIR FORCE ENGINEERING & SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

81 6 23 025

NOTICE

Please do not request copies of this report from
HQ AFESC/RD (Engineering and Services Laboratory).
Additional copies may be purchased from:

National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

Federal Government agencies and their contractors
registered with Defense Technical Information Center
should direct requests for copies of this report to:

Defense Technical Information Center
Cameron Station
Alexandria, Virginia 22314

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ESL/TR-81-09	2. GOVT ACCESSION NO. AD-A100 525	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CORRELATION OF SOOT FORMATION IN TURBOJET ENGINES AND IN LABORATORY FLAMES		5. TYPE OF REPORT & PERIOD COVERED Final Report August-September 1980
7. AUTHOR(s) Robert K. Gould Douglas B. Olson Hartwell F. Calcote		6. PERFORMING ORG. REPORT NUMBER AeroChem TP-407
9. PERFORMING ORGANIZATION NAME AND ADDRESS AeroChem Research Laboratories, Inc. P.O. Box 12 Princeton, New Jersey 08540		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE: 62601 JON: 1900-20-51
11. CONTROLLING OFFICE NAME AND ADDRESS Engineering and Service Laboratory Air Force Engineering and Services Center Tyndall Air Force Base, Florida 32403		12. REPORT DATE February 1981
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Air Force Office of Scientific Research Bolling Air Force Base Washington, DC 20332		13. NUMBER OF PAGES 67
15. SECURITY CLASS. (if this report) UNCLASSIFIED		
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Availability of this report is specified on verso of front cover		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Jet Fuels Soot Formation Fuel Structure Smoke Point		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Data obtained from aviation gas turbine combustor tests have been examined to determine the effects of fuel properties on soot-related measurements such as engine smoke number, combustor flame radiation, and/or combustor liner temperature. Some tests of smaller laboratory combustors used to simulate these large combustors were also examined. From the existing data it is clear that soot production is a strong function of the fuel chemical composition. Variations in the physical properties of the fuel do not correlate well with soot-related effects. In studies in which a broad range of fuel properties was examined.		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. (CONCLUDED)

correlation of soot-related effects with basic fuel compositional parameters including (1) the hydrogen content of the fuel, (2) the aromatic content of the fuel, and (3) the amount of multiple-ring aromatics in the fuel show that typically only the first of these correlates well. However, it has also been shown that fuel compositions can be chosen for which this correlating parameter fails.

In addition to examining the ability of basic compositional information to correlate with soot-related effects, the correlation of these effects with the reciprocal of the fuel smoke point was examined. The correlation of this simple empirical laboratory measurement with sooting was typically similar to that obtained with hydrogen content although in some cases where the hydrogen content did poorly, the reciprocal smoke point did well.

To reduce small-scale laboratory flame data on soot thresholds (including ASTM smoke point measurements) to a form which allows measurements taken on various laboratory apparatus to be compared with one another and with engine test results, a threshold soot index (TSI) based on smoke point data for pure compounds is defined and described. Once defined for pure compounds, TSI's can be calculated for fuel mixtures by using weighted sums of the TSI's of the fuel components if sufficient compositional information is available. Although only crude estimates of fuel TSI's can be made for the fuels used in most of the tests surveyed, correlations of these estimated fuel TSI's with soot data indicate that even crudely calculated TSI's do as well as other correlating parameters used to predict sooting behavior of fuels. Laboratory and large-scale experiments are needed to determine if accurate fuel TSI's can provide much improved predictions of the soot production from highly aromatic, out-of-specification fuels.

Correlation parameters of reciprocal smoke point or fuel TSI with soot-related effects were found to be > 0.9 in several tests. However, in several recent studies which appear to be quite extensive, these fuel parameters as well as hydrogen content all produced correlations of < 0.8 . The reasons for such poor correlations are unclear. Recommendations are made for tests to further examine this lack of consistency.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

The work reported herein represents a special study undertaken in conjunction with an ongoing laboratory study of the mechanism of soot nucleation in flames which is supported by the Air Force Office of Scientific Research (AFOSR). Additional funds to cover this work during the period 1 August through 30 September 1980 were provided by the Air Force Engineering and Services Center, Engineering and Services Laboratory (ESL), Tyndall Air Force Base, Florida. The program manager representing ESL was Captain Harvey J. Clewell, and the program manager representing AFOSR was Bernard T. Wolfson.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

Harvey J. Clewell III
HARVEY J. CLEWELL III, Capt, USAF, BSC
Air Quality Research Chemist

John T. Slankas
JOHN T. SLANKAS, Major, USAF
Chief, Environmental Sciences Branch

Michael G. MacNaughton
MICHAEL G. MACNAUGHTON, Lt Col, USAF, BSC
Chief, Environics Division

Francis B. Crowley III
FRANCIS B. CROWLEY III, Colonel, USAF
Director, Engineering & Services Laboratory

Accesision For	
NTIS STAN	<input checked="" type="checkbox"/>
DRDC T	<input type="checkbox"/>
Unpublished	<input type="checkbox"/>
Journalization	<input type="checkbox"/>
By	
Distribution	
Availability Codes	
Dist	Avail and/or Special
A	

TABLE OF CONTENTS

Section	Title	Page
I.	INTRODUCTION	1
II.	REVIEW AND ANALYSES OF THE DEPENDENCE OF GAS TURBINE COMBUSTOR SOOT PRODUCTION ON FUEL PROPERTIES	6
III.	LABORATORY STUDIES OF SOOTING FLAMES	19
IV.	RELATIONSHIP BETWEEN LABORATORY STUDIES OF SOOT AND LARGER SCALE TESTS.	21
V.	CONCLUSIONS AND RECOMMENDATIONS	24
	REFERENCES	27
APPENDIX		
A	EFFECT OF MOLECULAR STRUCTURE ON INCIPIENT SOOT FORMATION	29

LIST OF FIGURES

Figure	Title	Page
1	Comparison of Fuel Hydrogen Content and Reciprocal Smoke Point as a Soot Predictor for the J57 Combustor	9
2	Comparison of Fuel Hydrogen Content and Reciprocal Smoke Point as a Soot Predictor for the T63 Combustor	10
3	Comparison of Fuel Hydrogen Content and Reciprocal Smoke Point as a Soot Predictor for the TF41 Combustor	11
4	Comparison of Smoke Numbers Produced in Two Engines Using Similar Series of Fuels	16

LIST OF TABLES

Table	Title	Page
1	Selected Reports Describing Effects of Fuel on Soot Pro- duction in Jet Engine Combustors	3
2	Correlations of Soot-Related Measurements with Hydrogen Content and Reciprocal Smoke Point. High Power Conditions .	7

LIST OF TABLES (CONCLUDED)

Table	Title	Page
3	Correlations of Soot-Related Measurements with Fuel H Content and Reciprocal Smoke Point, Low Power Conditions . . .	12
4	Correlations of Soot-Related Measurements with Fuel Aromatics and Multiple-Ring Contents Under High Power Conditions	13
5	Correlations of Liner Temperature with Fuel Properties High Power Conditions	15
6	Correlations of Smoke Numbers Measured in Different Combustors for a Set of Fuels	15
7	Multiple Variable Regression Fits to Soot Data Under High Power Conditions	18
8	Comparison of Hydrogen Content, Reciprocal Smoke Point, and Threshold Soot Index Correlation with Engine Sooting. . .	23
9	Average Correlations of Hydrogen Content, Reciprocal Smoke Point, and Threshold Soot Index for Selected References . .	23

SECTION I

INTRODUCTION

Economic and availability factors are forcing a trend toward increased use of out-of-specification jet fuels. In particular, increased use of petroleum fractions with high aromatic contents is likely, and the prospect exists of substantial reliance on shale, tar sand, and coal derived fuels in the future. The tendency of these fuels to increase exhaust emissions and reduce engine performance and reliability has been the subject of increasing interest (References 1 to 11) over the last twenty years. Several reviews of the subject have recently been published (References 12 to 15).

In this work the literature describing several investigations of fuel effects on the performance of jet aircraft combustors (References 1 to 11) and on smaller stirred reactor combustors used to simulate these systems (References 1, 10, 16 to 19) has been examined. The goal of this review is to learn which fundamental fuel properties determine, or at least correlate well with, the tendency of highly aromatic fuels to form soot. Of course, the workers responsible for the cited efforts have attempted to do precisely this for their own results and have, in the process, focused attention on several fuel properties which appear to be important in soot production and emission. What is hoped for here is that by examining a broad range of tests and experiments from a variety of sources it will be possible to:

- (1) Select more universal criteria for predicting the extent of sooting from out-of-specification fuels.
- (2) Point the way to what additional work would be useful in refining these criteria or developing better ones.

The approach in this study has been to be selective rather than exhaustive, and it should be pointed out that time and money restrictions precluded consideration of all available studies. Much of the relevant work is in the report literature and therefore is not immediately accessible on a short time scale. Examination of a large volume of literature relating to fuel effects on gas turbines has focused, in this effort, on those papers which include a detailed examination of the physical and chemical properties (the independent variables) of the fuels used and measurements of either smoke emission or

related phenomena such as flame radiation or combustor liner temperatures (the dependent variables) (References 1 to 11, 16 to 19). Further concentration was made in this examination on those studies which tested a large enough variety of fuels to yield reasonable statistics. As a result of this selection process, the reports described in Table 1 have been closely examined. The first of these tabulated data sources is a study by Schirmer, McReynolds, and Daley (Reference 1) using a J57 can-type combustor. In this study an aromatic-free JP-5 was used as the base fuel with triethyl benzene (single-ring aromatic) and methyl naphthalene (double-ring aromatic) additions of up to 1% (volume). In addition, decalin (a double-ring saturated compound), tetralin (a double-ring partially saturated compound), iso-octane, n-heptane, and JP-4 were tested. The measured dependent variables were the flame radiation in the primary combustion zone and the combustor liner temperature.

Naegeli and Moses (Reference 10) measured flame radiation, smoke number, and liner temperature in a T63 can combustor using JP-5 as a base fuel to which aromatics were added. Also a Jet A, synthetic JP-5's from shale, coal, and tar sands, and marine diesel fuel were tested. In another paper (Reference 19), these authors described a smaller set of experiments in which Jet A was blended with xylenes, decalin, methyl naphthalene, tetralin, and anthracene to produce a series of fuels all with a hydrogen content of 12.8% (wt). These experiments were performed in a small 2-inch Phillips Combustor where flame radiation was measured. Although the number of fuels tested is not as large in this study as in others, the constraint on H content makes this study notable.

Two reports by Gleason et al. (References 6, 7) and a similar report by Vogel et al. (Reference 8) describe a series of tests for a J79 combustor (Reference 6), a F101 combustor (Reference 7), and a TF41 combustor (Reference 8). The base fuel in these studies was JP-4 to which xylenes, naphthalenes, and mineral oil were added. A very similar series of fuels was used for all of the tests in these three combustors. A variety of independent variables was measured including smoke number, smoke emission (g/kg), and liner temperature. The reports extensively analyze the results to determine how well these soot-related quantities correlate with numerous fuel properties over a wide range of operating conditions.

TABLE 1. SELECTED REPORTS DESCRIBING EFFECTS OF FUEL ON SOOT PRODUCTION IN JET ENGINE COMBUSTORS

Ref.	Combustor	Soot-Related Measurements	Inlet Pressure Range, atm	Description of Fuels
1	J57	Flame radiation, liner temperature	5.0-15.0	Twelve fuels including aromatic-free JP-5, JP-5 blended with triethyl benzene and methyl naphthalene, JP-4, decalin, tetralin, iso-octane, n-heptane, kerosene.
10	T63	Flame radiation, liner temperature	2.3-4.7	Eighteen fuels including Jet A, JP-5, JP-5 blended with monocyclic and bicyclic aromatics, synthetic JP-5's, JP-5 blended with diesel fuel, JP-5 blended with decalin, diesel fuel, leaded gasoline. (Data using leaded gasoline were excluded from this report.)
19	2-inch combustor	Flame radiation	5.0-10.5	Eight fuels including Jet A, Jet A blended with xylenes, decalin, methyl naphthalene, anthracene, tetralin.
6	J79	Flame radiation, liner temperature, smoke number, smoke emission	2.4-12.4	Thirteen fuels including JP-4, JP-8, and blends of these with xylenes, and naphthalenes and mineral oil, diesel fuel.
7	F101	Flame radiation, liner temperature, smoke number, smoke emission	3.9-12.4	
8	TF41	Flame radiation, liner temperature smoke number, smoke emission	2.9-18.5	

All these reports demonstrate clearly that the physical properties (viscosity, density, surface tension, vapor pressure, boiling points) of the fuels have, at most, secondary effects on sooting behavior. Therefore, these workers have concentrated their efforts on examining soot production (or a related quantity such as flame radiation or smoke number) as it varies with chemical properties of the fuel. In particular, attention was concentrated on the following chemical properties of the fuels as measured by the report authors: (1) hydrogen content, (2) aromatic content, and (3) amount of multiple-ring aromatics. A fourth fuel property, the fuel smoke point,* also was considered. The first of these independent variables has been demonstrated to often correlate very well with soot-related combustor measurements (References 4, 5, 10). Indeed, hydrogen content is most commonly judged the fundamental property of choice in predicting the tendency of a fuel to produce soot. It is striking that such a crude measure of the chemical makeup of the fuel does so well as an indicator of the propensity of a fuel to form soot.

Aromatic content has long been known to be a cause of soot formation. For typical fuel blends, it often correlates with hydrogen content, of course, but typically it is found to correlate less well with soot production than does hydrogen content (see, e.g., References 6, 7, and 8 and the following section). In Reference 1 it is shown that increasing the multiple-ring aromatic content of a fuel is very effective in producing a large increase in flame radiation (beyond that observed with an equivalent amount of a single-ring aromatic). This is examined more closely below.

Finally, the importance of fuel smoke point as a means of predicting soot-ing behavior has been examined. Although it has not been widely noted, when this is done it is found that the reciprocal of the smoke point is typically as good and, in some cases, a considerably better predictor of sooting than the hydrogen content. The objection is sometimes made that, whereas the first three variables listed above are fundamental properties of a fuel capable of being predicted or unambiguously measured in repeatable, standardized ways, the smoke point of a fuel is an empirical quantity, which although a

* The smoke point of a fuel is the minimum height of a small laboratory diffusion flame, burning the fuel in air, at which luminosity at the flame tip from soot formation is observed. The standardized apparatus and procedure are described in Reference 20.

standardized ASTM test is defined (Reference 20), is nonetheless ambiguous in the sense that it has historically been dependent on the type of burner employed in the test (see, e.g., References 1 and 21). It will be shown here that this objection can be removed by defining an index based on the smoke point which unambiguously defines the sooting tendency of a fuel regardless of which sort of diffusion flame burner is used to measure the smoke point. An objection can also be made to using a smoke point defined by using small laboratory diffusion flames to indicate the sooting tendency of fuels in highly turbulent combustors which are generally treated as well-stirred combustors in which premixed flames are burning. However, in the context of soot production, the extent to which engine combustion chambers can be considered well stirred is questionable in view of the very low overall fuel/air ratios which yield soot in these systems. Fuel-rich flamelets which produce soot unquestionably occupy some fraction of the combustor dome and primary combustion volumes and to this extent diffusion flame-derived quantities such as the smoke point might, and indeed do, correlate well with soot production in these practical systems. Furthermore, a conceptual problem in the relating of smoke point and sooting in large combustors is that measurement of smoke point is a measurement of the threshold at which sooting commences. On the other hand, in large combustors, the soot yield or a quantity dependent on yield is measured. That a good correlation exists between these two quantities is a reflection of the tendency of fuels which have low thresholds to produce more soot at a given equivalence ratio than fuels with high thresholds (Reference 22). It may also be due to the fact that in a large combustor one is dealing with a large ensemble of small partially mixed diffusion flamelets of various sizes for which, at any given moment, a fraction will be of small enough scale or at low enough equivalence ratio to be below soot threshold. The soot yield will then vary with the fraction which burns beyond threshold and thus the correlation is established.

In the sections which follow, first the pertinent data from the selected references will be examined. Then laboratory data on small sooting flames will be described from which the tendency to soot based on the smoke point measurement will be quantified and shown to be an unambiguous property of the fuel or compound measured. In the last sections the implications of the comparison of full-scale and laboratory smoke measurements will be discussed and recommendations made for further work.

SECTION II

REVIEW AND ANALYSES OF THE DEPENDENCE OF GAS TURBINE COMBUSTOR SOOT PRODUCTION ON FUEL PROPERTIES

As can be seen from selected reports of Table 1, a wide variety of aviation gas turbine combustion systems has been tested. Most of the selected studies have been extensive, involving more than ten fuel blends, a large range of operating conditions, and a wide variety of measurements which include, in addition to soot-related quantities, determination of NO_x , CO, and unburned hydrocarbon emission, combustion efficiency, relight tests, and other performance parameters which might be a function of fuel properties. The reader is directed to the cited reports for details on measurement techniques and results.

Analyses of the data in the selected reports has generally led to the conclusion that fuel hydrogen content (H%) and smoke points (SP) of the fuels (as measured by the report authors using ASTM procedures) are the best indicators of soot production in both large- and small-scale combustors. Table 2 lists the correlations* between soot-related variables, flame radiation, or smoke number, and these two fuel properties at high operating power levels for the selected studies. The correlation between the H content, H%, and the reciprocal of the smoke point, $(\text{SP})^{-1}$, is also given, as well as the ranges for these fuel variables and the engine operating conditions (the fuel/air weight ratio and the burner inlet pressure). From the data of Table 2, it would appear that, at most, only slightly better correlations occur between the soot-related quantity and $(\text{SP})^{-1}$ as opposed to H%. However, for all but the data from References 10 and 19, there is no firm statistical criterion for choosing between these

* The correlation between two ordered sets of numbers $\{y_i\}$ and $\{x_i\}$ is a measure of the degree to which one variable appears to vary with or depend on the other. The correlation, r , is given by

$$r = \left\{ \frac{\overline{xy} - \overline{x}\overline{y}}{\sigma(x)\sigma(y)} \right\}^{1/2}$$

where σ is a standard deviation and bars over a variable indicates an average value. If a plot of points (y_i, x_i) all lie on a straight line, $r = +1$ or -1 . Scatter about a best fit line results in $|r| < 1$. The smaller $|r|$ is the greater the scatter.

TABLE 2. CORRELATIONS OF SOOT-RELATED MEASUREMENTS WITH HYDROGEN CONTENT AND RECIPROCAL SMOKE POINT
HIGH POWER CONDITIONS

Reference/ Combustor	Dependent Variable	Fuel Property/ Dependent Variable ^a		Ranges of Fuel Properties		Operating Conditions	
		H%	(SP) ⁻¹	Correlation between H% and (SP) ⁻¹		F/A g/kg	p, atm
				H%	(SP) ⁻¹		
1/J57	Flame radia- tion at dome	- 0.98	0.98	- 0.96	9.1-14.0	< 0.02-0.17	15 15 High power
10/T63	Flame radia- tion at dome	- 0.91	0.94	- 0.88	12.0-14.3	0.039-0.084	20 4.7 Full power
19/2-inch combustor	Radiation index ^c	- 0.81	0.95	- 0.86	12.8-14.2	0.042-0.080	8-24 5-15 Data averaged over range
✓ 6/J79	Smoke number ^d	- 0.65	0.72	- 0.97	12.0-14.5	0.031-0.083	20 12.4 Sea-level takeoff
7/F101	Smoke number	- 0.71	0.70	- 0.97	12.0-14.5	0.031-0.083	29 12.4 Sea-level takeoff
8/TF41	Smoke number	- 0.73	0.73	- 0.97	11.9-14.4	0.026-0.083	21 18.5 Sea-level takeoff

^a Independent variables are hydrogen content, H%, and the inverse of the reciprocal smoke point for the fuels, $(SP)^{-1}$, mm^{-1} .

^b Burner inlet pressure.

^c This index with ratio of combustor radiation for the test fuels relative to that observed using a Jet A base fuel.

^d SAE smoke number, see Reference 23.

two fuel properties since they correlate so well with one another. The fuels studied in Moses and Naegeli's work were such that the $H\%/(SP)^{-1}$ correlation is less good (in Reference 19, this was done purposely by choosing fuels of fixed H% but varying SP) and in these tests the correlation of soot with inverse smoke point is clearly superior. In Figures 1 and 2, comparisons between H% and $(SP)^{-1}$ are shown graphically for the data of References 1 and 10. These figures were prepared by performing best fits of the independent variables H% or $(SP)^{-1}$ to the dependent soot related, measured variables of Table 2. These best fit functions are then used to obtain the predicted values of the dependent variable which are compared to observed values in these figures.

It is disturbing that in the very complete series of tests of References 6, 7, and 8 all the correlations are relatively poor. Figure 3 (made using the TF41 data) makes this point very clear when compared to Figures 1 and 2. The engines tested in these three studies range from the older, sooting J79 through the more modern, but still relatively sooty TF41 to the modern, very clean burning F101. Despite the fact that the F101 burns very cleanly, the predicted decrease in liner life of this engine from the use of high aromatic fuels is almost as severe as that predicted for the J79. Thus, the impact of new fuels on liner life and reliability remains an important consideration and low correlations of fuel properties with sooting behavior are a matter of concern because of their implications with regard to the predictability of fuel property effects.

In Table 3 data from the same studies (using the same sets of fuels) under low power (idle) conditions are analyzed. The correlations tend to be slightly better under these operating conditions than those obtained at high power. There is, however, no difference apparent in the data between the H content and reciprocal smoke point as a correlating parameter. The fact that for the J79 and F101 systems the correlations are improved under idle conditions is not of much comfort since in these situations liner life is of little concern.

Table 4 shows the correlations of soot-related quantities measured under high power conditions (as tabulated above in Table 2) with aromatics and multiple-ring aromatics as the fuel-related variables. As can be seen by comparison with Table 2, neither of these fuel properties correlates as well with sooting behavior as do H content or reciprocal smoke points except in the instance of Reference 6 where the correlation of aromatics with smoke

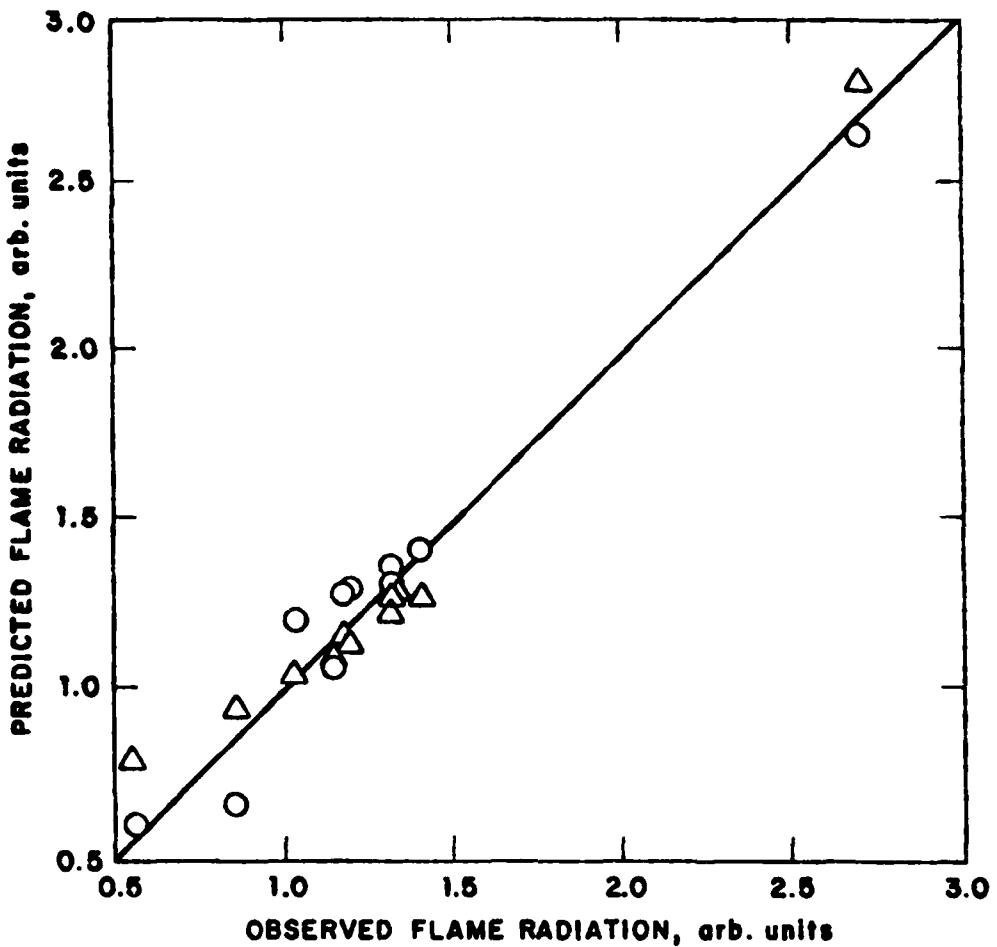


Figure 1. Comparison of Fuel Hydrogen Content and Reciprocal Smoke Point as a Soot Predictor for the J57 Combustor
(Reference 1)

○ - Correlation using H%, $r = -0.98$
 △ - Correlation using $(SP)^{-1}$, $r = 0.98$

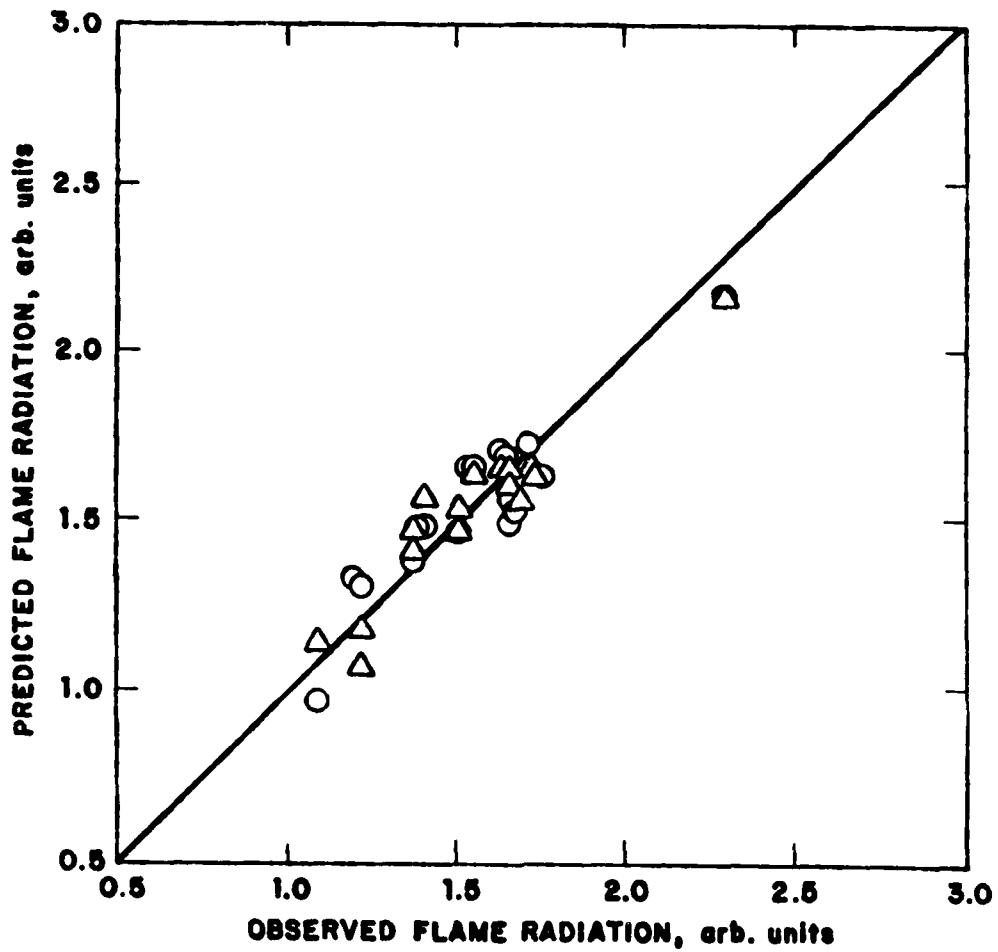


Figure 2. Comparison of Fuel Hydrogen Content and Reciprocal Smoke Point as a Soot Predictor for the T63 Combustor
 (Reference 10)

\circ - Correlation using $H\%$, $r = -0.91$
 Δ - Correlation using $(SP)^{-1}$, $r = 0.94$

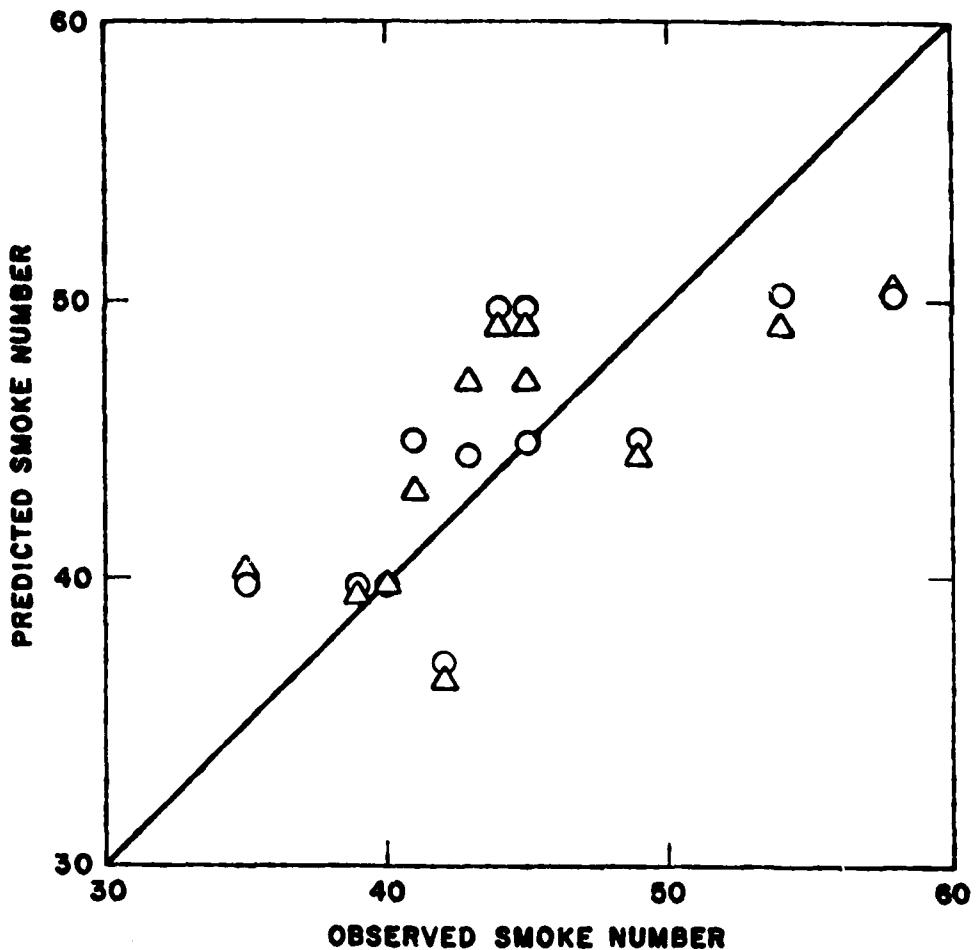


Figure 3. Comparison of Fuel Hydrogen Content and Reciprocal Smoke Point as a Soot Predictor for the TF41 Combustor
(Reference 8)

○ - Correlation using H%, $r = -0.73$
 △ - Correlation using $(SP)^{-1}$, $r = 0.73$

TABLE 3. CORRELATIONS OF SOOT-RELATED MEASUREMENTS WITH FUEL H CONTENT AND RECIPROCAL SMOKE POINT
LOW POWER CONDITIONS

Reference/ Combustor	Dependent Variable	Fuel Property/ Dependent Variable		Correlation between H% and (SP) ⁻¹	Ranges of Fuel Properties		Operating Conditions			
		Correlations			H%	(SP) ⁻¹	F/A	P, atm	Description	
		H%	(SP) ⁻¹		H%	(SP) ⁻¹	g/kg	g/kg		
1/J57	Flame radius- tion at dome	- 0.98	0.99	- 0.96	9.1-14.0	0.02-0.17	10	5	Low power	
10/T63	Flame radi- tion at dome	- 0.89	0.90	- 0.88	12.0-14.3	0.039-0.083	12	2.8	25% of full power	
6/J79	Smoke number	- 0.95	0.92	- 0.97	12.0-14.5	0.039-0.083	9.4	2.4	Idle	
7/F101	Smoke number	- 0.84	- 0.77	- 0.97	12.0-14.5	0.031-0.083	14	3.9	Idle	
8/TF41	Smoke number	- 0.88	0.86	- 0.97	11.9-14.4	0.026-0.083	14	2.9	Idle	

TABLE 4. CORRELATIONS OF SOOT-RELATED MEASUREMENTS WITH FUEL AROMATICS AND MULTIPLE-RING CONTENTS
UNDER HIGH POWER CONDITIONS

Reference / Combustor	Fuel Property/ Dependent Variable	Correlations		Correlation between Ar and M-R Ar		Ranges of Fuel Properties		Operating Conditions	
		Dependent Variable	Ar, %	M-R Ar, %	Ar, %	M-R Ar %	F/A g/kg	P, atm	Description
1/J57	Flame radiation at dome	0.93	0.069	-0.11	0-94 ^a	0-8.5 ^a	15	15	High power
10/T63	Flame radiation at dome	0.89	0.83	0.79	8.1-37.8 ^b	0-9.4 ^b	20	4.7	Full power
19/2-inch combustor	Radiation index	0.70	0.74	0.30	8.1-33.8 ^b	1.3-20.1 ^b	8-24	5-15	Data averaged over range
13	Smoke number	0.42	0.79	0.17	12.2-63.4 ^a	0.6-24.6 ^a	20	12.4	Sea-level takeoff
6/J79	Smoke number	0.59	0.56	0.17	12.2-63.4 ^a	0.6-24.6 ^a	29	12.4	Sea-level takeoff
7/F101	Smoke number	0.70	0.36	0.22	11.4-59.1 ^a	0.6-24.8 ^a	21	18.5	Sea-level takeoff
8/TF41									

^a Volume %

^b Weight %

number is greater than that of any of the other fuel properties. This exception is in all likelihood accidental, however, and its value, 0.79, is not large in any case. Data on aromatic content and soot taken under low power conditions show these correlations to also be lower than those found using H content and reciprocal smoke point.

As noted above, for most combustors the increase in liner temperature which accompanies soot radiation is a cause for concern. The question thus arises of how well the liner temperature correlates with the four fuel properties selected for examination and how well liner temperature correlates with the other soot-related properties of Tables 2 to 4. These correlations are given in Table 5 for the combustors of References 1, 6, 7, and 8 at the high power levels of Tables 2 and 4. From Table 5, it is clear that the H content is a slightly better correlating parameter than the other fuel properties examined. Reciprocal smoke point is better than aromatic content. Multiple-ring aromatics seem to play little role. Again for the J79, F101, and TF41 studies (References 6, 7, and 8), none of the parameters are exceptionally good. Furthermore, the correlation of peak liner temperature with smoke number is low in these last three studies. In short, in these studies, not only do none of the fuel properties correlate exceptionally well with soot-related measurements, but the soot-related quantities (e.g., combustor liner temperature, engine smoke number) do not correlate well with one another. To further emphasize this point, examination of data taken under engine idle conditions shows the correlations corresponding to those of Table 5 to be even weaker. As a flagrant example, one finds from Reference 7 that the correlation of smoke number to peak liner temperature is -0.43 for the F101 engine under idle conditions apparently indicating that in this case the role of soot radiation in determining liner temperature is minimal for this engine under idle conditions.

An additional way of examining the data involves determining whether a particular set of fuels used in different engines soots in a consistent way. That is, does the amount of soot produced in one engine by a fuel correlate well with the amount of soot that fuel produces in another engine operating under comparable conditions, relative to that produced in the engines by some reference fuel? References 6, 7, and 8 allow this hypothesis to be checked. These studies used nearly identical series of fuels. One fuel (Fuel No. 4, a JP-8, xylenes blend) used in the Reference 8 study (which corresponds to

Fuel No. 10 of References 6 and 7) seems way out of line and has been excluded. In Table 6, the correlation of smoke numbers measured using this series of fuels is shown, and in Figure 4 an example of the comparison between the J79 and TF41 data is shown. As can be seen from Figure 4, a lot of scatter exists. Thus, the correlations are not strikingly large, but are possibly significant in view of the low correlation found between all the measurements of *soot* in these studies.

TABLE 5. CORRELATIONS OF LINER TEMPERATURE WITH FUEL PROPERTIES
HIGH POWER CONDITIONS^a

Reference/ Combustor	Correlations of Liner Temperature with Fuel Properties ^b				Correlation between Liner Temperature and Radiation Smoke Number ^c
	H%	$(SP)^{-1}$	Ar, %	M-R Ar, %	
1/J57	- 0.98	0.92	0.85	0.12	0.97
6/J79	- 0.89	0.83	0.83	0.44	0.42
7/F101	- 0.65	0.59	0.59	0.43	0.64
8/TF41	- 0.69	0.64	0.61	0.46	0.62

^a See Table 2 or 4 for fuel air ratio and inlet pressures. Liner temperatures are the temperature differences between the inlet and peak liner temperatures observed.

^b See Tables 2 and 4 for ranges of fuel properties.

^c Radiation or smoke number volume are those used to obtain correlation.

TABLE 6. CORRELATIONS OF SMOKE NUMBERS MEASURED IN DIFFERENT COMBUSTORS
FOR A SET OF FUELS^a

Ranges of Smoke Numbers			Correlations between Combustors		
J79	F101	TF41	J79/F101	J79/TF41	F101/TF41
55.2-88.9	2.6-4.7	35-57	0.68	0.56	0.60

^a From References 6, 7, and 8. All at sea-level takeoff operating condition.

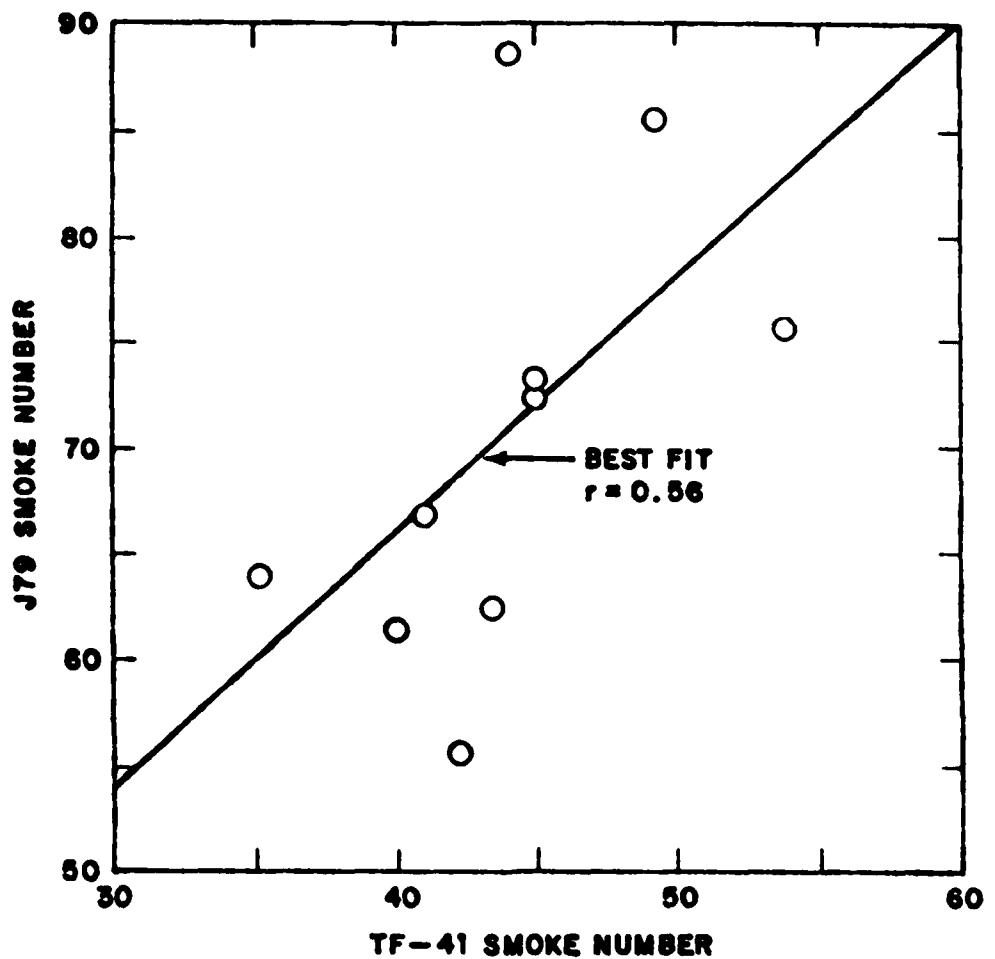


Figure 4. Comparison of Smoke Numbers Produced in Two Engines
Using Similar Series of Fuels

In a final attempt to find improved correlating parameters, it was deemed worthwhile to examine multiple variable linear regressions in which two or more fuel properties are used in linear combination to produce best fits to the soot data. Since multiple-ring aromatics are known to increase soot formation dramatically in laboratory flames (see below) and in large combustors (see Reference 1), the data of the selected reports were fit with multiple variable linear regressions using the pairs of independent variables (H content, multiple-ring aromatic content and inverse smoke point, multiple-ring aromatic content). The correlations achieved by fitting multiple-variable linear equations of the forms

$$\text{soot-related quantity} = a_0 + a_1(\text{H}\%) + a_2(\text{M-R Ar, \%})$$

$$\text{or} \quad \text{soot-related quantity} = b_0 + b_1(\text{SP}^{-1}) + b_2(\text{M-R Ar, \%})$$

to the data are shown and compared to single variable correlations in Table 7. Table 7 shows that, in most cases, little is gained by this multiple-variable approach. (In the study described in Reference 8 a more extensive attempt at applying multiple-variable regressions to the data set led to the same conclusion.) Only in the case of the J79 data (Reference 6) is a dramatic increase in the quality of the fit noted. The failure of the multiple-variable approach to help significantly in most cases is twofold. First multiple-ring aromaticity in these studies often does not correlate very well with sooting and, secondly, where it does, it also correlates well with H% and $(\text{SP})^{-1}$. Thus, its inclusion is not very helpful.

Similar efforts in which other combinations of fuel properties are tried generally do less well than the combinations of Table 7. Of course, increasing the number of independent variables which are simultaneously fit tends to increase the correlation coefficient simply by decreasing the statistical degrees of freedom. More sophisticated statistical tests (the F-test) are then needed to determine whether the better correlation obtained using more than one variable is a true improvement or simply a mathematical artifact. Such an examination is not included, but it seems likely that only in the case of the J79 data is a true improvement to be made by correlating more than one variable. Even in this case use of three or four of the fuel properties simultaneously provided no significant further advantage, e.g., a correlation of only 0.84 is achieved by using all four fuel properties in a multiple linear regression fit to these data.

TABLE 7. MULTIPLE VARIABLE REGRESSION FITS TO SOOT DATA
UNDER HIGH POWER CONDITIONS

Reference/ Combustor	Single-Variable Correlations			Multiple-Variable Correlations	
	H%	$(SP)^{-1}$	M-R Ar, %	H%/M-R Ar%	$(SP)^{-1}/M-R Ar\%$
1/J57	- 0.98	0.98	0.07	0.98	0.99
10/T63	- 0.81	0.95	0.74	0.96	0.95
19/2-inch combustor	- 0.91	0.94	0.83	0.93	0.96
6/J79	- 0.65	0.72	0.79	0.84	0.84
7/F101	- 0.71	0.70	0.56	0.75	0.72
8/TF41	- 0.73	0.73	0.36	0.73	0.73

SECTION III

LABORATORY STUDIES OF SOOTING FLAMES

Laboratory studies of soot thresholds in small premixed and diffusion flames have traditionally suffered from the lack of a method of comparing results of one study with those of other studies. The standardization of laboratory diffusion flame measurements (Reference 20) to allow smoke points to be obtained in a repeatable way is an attempt to get around this problem. However, what has been needed is a means of reducing or removing altogether the influences of geometry and fluid mechanical processes occurring in these small flames so that soot threshold for a fuel can be assigned based only on the chemical structure of that fuel. Such a method is presented in Appendix A. In the paper presented in Appendix A, it is shown that data from laboratory studies can be compared in such a way that fuel compounds can be assigned a number which specifies the sooting tendency of that compound. This threshold soot index (TSI) appears to be assignable to a wide variety of compounds with an accuracy of $\pm 10\%$.

For premixed flames, the TSI is directly proportional to the minimum equivalence ratio at which sooting occurs, ϕ_c

$$TSI = a - b \phi_c$$

For diffusion flames, the TSI is inversely proportional to the smoke point,

$$TSI = a' (MW) (SP)^{-1} + b'$$

where MW is the molecular weight of the fuel. The constants a and b and a' and b' are specific to the measurement apparatus and must be determined by calibration of each apparatus with at least two fuels having known TSI's. Tables of TSI's for a variety of pure fuel compounds are given in Appendix A.

Jet fuels are, of course, mixtures containing large numbers of compounds. Measurement of the diffusion flame smoke point in the laboratory, as indicated in the previous section, produces results which often correlate well with large scale engine results. However, as noted earlier, one objection to relying on fuel smoke point as an indicator of sooting tendency is that it is not a fundamental fuel property as are, for instance, the aromatic or hydrogen contents of the fuel. A major step toward making soot threshold information

reflect the chemical composition of the fuel and thus a fundamental, predictable property of the fuel is to define a fuel TSI based on the TSI's of the compounds making up the fuels. This can be done using either diffusion flame or premixed flame TSI's. The simplest approach is to make the fuel TSI a linear, weighted sum of the TSI's of the fuel constituents,

$$\text{Fuel TSI} = \sum x_i \text{TSI}_i$$

where x_i is either the weight, volume, or mole fraction of the i th constituent having TSI_i . This procedure has some basis in experimental work performed on sooting thresholds in the past. Minchin (Reference 24) examined a series of kerosenes having varying amounts of aromatics or naphthalenes and found that plots of the reciprocal smoke points of these kerosenes against the aromatic or naphthenic volume fraction produced straight lines. Thus, fuel TSI's calculated for these kerosenes could be used to predict their smoke points. The generality of the procedure and whether weight or mole fractions would produce better smoke point predictions need to be examined further. How well fuel TSI's calculated in this manner work in correlating sooting in engine combustors is examined below.

SECTION IV

RELATIONSHIP BETWEEN LABORATORY STUDIES OF SOOT AND LARGER SCALE TESTS

As detailed in Appendix A, it is possible to calibrate a wide variety of laboratory-scale diffusion or premixed flame burners so that if soot thresholds for a particular compound are obtained on a particular apparatus, the threshold for that compound on other apparatus is predictable. In other words, it is possible to calibrate out the fluid mechanical and geometric factors which affect the smoke point or onset equivalence ratio measurement and obtain a TSI for a compound which is dependent only on its chemical structure. Having obtained a useful definition for the TSI of a particular compound, it is natural to see if this can be used to form an index for fuels which correlates with smoke emissions observed in large scale tests.

Effective TSI values were computed for the fuels tested in References 1, 6, 7, 8, 10, and 19 for correlation with smoke number and flame radiation results. To do this one must first select whether premixed or diffusion flame TSI's are most applicable. Diffusion flame TSI's were selected since the spray fueled combustors all burn with many fuel-rich regions which must be diffusion-controlled. (Also, data on premixed flames are less complete and hence can be used with less certainty. This point should be examined in the future when a more complete data base is available, however.) Next TSI values must be assigned for base fuels and some of the hydrocarbon mixtures used in these studies. For example, in Reference 19, where pure components were used to adjust fuel properties, we must also consider Jet A and DFM. This procedure was accomplished using Reference 10 data which gives smoke points of several pure components along with JP-5, JP-4, and kerosene. For a first approximation, the variation in average molecular weights among the jet fuels was ignored and a linear least-squares fit of TSI's was performed for n-heptane, decalin, and tetralin to the Reference 10 smoke points. (This essentially calibrates the smoke point apparatus used.) Then using this fit, TSI's were estimated for jet fuels from smoke points. For most of the engine tests, fuel compositions were not known; only simplified analytical results on the concentration of single-ringed, double-ringed aromatic species, etc. were known. Average TSI values were assigned to these component classifications by referring to Table 3 in Appendix A.

This procedure is not at all unique and time restraints prevented more detailed, and possibly much better, TSI assignments.

It should be noted that, in cases of pure compounds, soot production which correlates well with $(SP)^{-1}$ will automatically correlate well with TSI since the two variables are so closely related. However, fuels are a blend of many compounds and, as noted in Section III, an assumption is being made that the TSI's of fuel blends can be calculated by simply calculating the weighted sums of the TSI's of the compounds or groups of compounds making up the fuel.

(For these calculations, weight fractions were used as weighting factors in the summations.)

Results of correlating computed average TSI's against experimental results are given in Table 8 along with summary results from the other correlations. Some average performance numbers are also given in Table 9. Overall the TSI correlation does as well as H% but not quite as well as $(SP)^{-1}$. It correlates flame radiation data better than smoke number values (as do H% and $(SP)^{-1}$). In fairness to TSI efforts we note that only from References 1 and 19 was detailed fuel composition information of the type needed to calculate accurate TSI's available. In the former case, TSI does as well as the other two fuel variables; in the latter case, the TSI correlation does appreciably better than $(SP)^{-1}$ and much better than H%. In the other cases estimates were made of average TSI's for broad classes of compounds. This may be at least partly responsible for the lack of strong correlation between fuel TSI and sooting in these cases.

TABLE 8. COMPARISON OF HYDROGEN CONTENT, RECIPROCAL SMOKE POINT, AND THRESHOLD SOOT INDEX CORRELATION WITH ENGINE SOOTING

Reference/ <u>Combustor</u>	Soot-Related <u>Variable</u>	Operating Condition	Correlation		
			H%	(SP) ⁻¹	TSI
1/J57	Flame radiation	High power	- 0.98	0.98	0.98
1/J57	Flame radiation	Low power	- 0.98	0.99	0.99
10/T63	Flame radiation	Full power	- 0.91	0.94	0.88
10/T63	Flame radiation	25% of full power	- 0.89	0.90	0.87
19/2-inch combustor	Radiation index	Averaged over range	- 0.81	0.95	0.98
6/J79	Smoke number	Sea-level takeoff	- 0.65	0.72	0.63
6/J79	Smoke number	Idle	- 0.95	0.92	0.94
7/F101	Smoke number	Sea-level takeoff	- 0.71	0.70	0.57
7/F101	Smoke number	Idle	- 0.84	0.77	0.83
8/TF41	Smoke number	Sea-level takeoff	- 0.73	0.73	0.72
8/TF41	Smoke number	Idle	- 0.88	0.86	0.86

TABLE 9. AVERAGE CORRELATIONS OF HYDROGEN CONTENT, RECIPROCAL SMOKE POINT, AND THRESHOLD SOOT INDEX FOR SELECTED REFERENCES

Category	Average Correlations		
	H%	(SP) ⁻¹	TSI
High power measurements, References 1, 10, 19, 6, 7, 8. From Tables 2 and 8.	- 0.79	0.83	0.79
Low power measurements, References 1, 10, 19, 6, 7, 8. From Tables 3 and 8.	- 0.91	0.89	0.90
Flame radiation, References 1, 10, 19. From Tables 2, 3, and 8.	- 0.91	0.95	0.94
Smoke number, References 6, 7, and 8. From Tables 2, 3, and 8.	- 0.78	0.78	0.76
Overall	- 0.84	0.86	0.84

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

A number of data sets obtained on a variety of aircraft gas turbine and laboratory scale combustors have been examined to determine which, if any, chemical properties of jet fuels are reliable predictors of soot formation. For some data sets, certain fuel properties, notably hydrogen content and the reciprocal of the fuel smoke point, correlate very well (> 0.9) with the amount of soot or flame radiation observed. In other cases correlations are poor (< 0.8). Unfortunately, these latter cases involve tests of widely used and/or quite modern combustor systems [J79 (Reference 6), F101 (Reference 7), TF41 (Reference 8) combustors]. The problem appears serious since, even for combustors such as the F101 which are very "clean", sizable ($\approx 50\%$) decreases in combustor liner lifetime are predicted for the sootier fuels.

A fuel property defined in this report, the threshold soot index or TSI, is based on the smoke points of fuel components. The TSI of a fuel is defined as the sum of the TSI's for the compounds making up the fuel times the weight fraction of that compound in the fuel. For some of the data sets, particularly those where a great deal is known about the specific compounds making up the fuel, the TSI correlation appears to do as well or better than $H\%$ of $(SP)^{-1}$. Where both $H\%$ and $(SP)^{-1}$ do poorly as predictors, TSI also fails.*

It has been widely noted that the chemical composition, not the physical properties of a fuel, appears to dominate the formation of soot in these combustors (see especially References 5, 10, and 12). However, the results to date do not allow one to pick between fuel properties such as hydrogen content, or reciprocal smoke point as a superior predictor of sooting behavior since typical series of fuels tested were not selected to produce independent variation of these properties. In only two data sets was the correlation between the hydrogen content and $(SP)^{-1}$ below 0.95 (see Table 2). For these two data sets where

* This is to be expected since, by its definition, the TSI is very closely related to the reciprocal smoke point. It differs from the reciprocal smoke point mainly in that, like the hydrogen content, it is a property which can be predicted for a fuel (assuming the fuel composition is known) whereas the smoke point must be measured.

the two variables were poorly correlated, $(SP)^{-1}$ was a better predictor of soot-ing (more precisely, flame radiation). For one of these sets (Reference 19) the fuels were purposely blended to make H% a poor correlator. However, the value of a correlation is to a large extent based on its ability to work in exceptional cases. Based on this, $(SP)^{-1}$ currently appears superior.

TSI has the potential to be a better predictor than H% and is more readily useful than $(SP)^{-1}$, but more precise fuel composition measurement is needed to test this. In References 1 and 19, where pure compounds were used as additives, TSI does better than H%. Its failure to do as well in other tests may well be due to our inability to calculate it correctly since the fuel composition information available is known only with regard to broad classes of compounds which can have widely varying TSI's within themselves. TSI would be expected to be more valuable than $(SP)^{-1}$ because the TSI is a calculable property like H% and can thus be used to design fuels without resorting to laboratory measurements of each possible blend. A useful set of experiments needed to make certain that this last statement is true would be to complement the data of Reference 19 (in which hydrogen content was fixed for all but the base fuel) by testing blends which have differing hydrogen contents but the same TSI's in small scale combustors like the Phillips Combustor and then in larger engine combustors.

The results of References 1, 10, and 19 show that the correlation between soot related effects and fuel composition can be very high. Thus, it is particularly troublesome that the recent series of tests described in References 6, 7, and 8 yielded such poor correlations between fuel composition and soot related effects. These latter experiments should be repeated using fuels with very well defined compositions to see if better predictability can be achieved. Experiments using blends of compounds with an aromatic-free base fuel, as in Reference 1, would be very helpful.

In this report the TSI of a fuel has been defined to be the weighted average of the component TSI's. This definition makes sense if the reciprocal smoke point of a fuel can also be calculated using the TSI's of the fuel components. Reference 24 indicates that this may be the case, but this additivity should be fully tested in the laboratory.

In the same vein, it may well be that computing TSI's of fuel blends using compound mole fractions rather than weight or volume fractions would produce more accurate predictions of blend smoke points and better correlations of TSI with engine soot data. This has not been tested but should be.

The smoke point and TSI of a fuel are based on laboratory measurements of the threshold at which sooting begins to occur. It may well be that a more complete knowledge of not just threshold behavior but soot yield above threshold for pure compounds and blends would lead to a more useful index for predicting soot yields in engines. Very little laboratory scale soot yield data exists, a situation which should be corrected.

If it should be found that, in fact, the TSI rather than the hydrogen content of a fuel is the important parameter, the practical significance is great. To know that fuel blends with olefinic and cyclic hydrocarbons produce less soot and flame radiation than blends of alkanes and aromatics, which have the same hydrogen content, would have obvious important implications for the refiner of jet fuels.

REFERENCES

1. Schirmer, R.M., McReynolds, L.A., and Daley, J.A., "Radiation from Flames in Gas Turbine Combustors," *SAE Trans.* 68, 554-561 (1960).
2. McClelland, C.C., "Effects of Jet Fuel Constituents on Combustor Durability," *Naval Air Propulsion Test Center, NAEC-AEL-1736*, May 1963.
3. Butze, H.F. and Ehlers, R.C., "Effect of Fuel Properties on Performance of a Single Aircraft Turbojet Combustor," *NASA TMX-71789*, October 1975.
4. Butze, H.F. and Smith, A.L., "Effects of Fuel Properties on Performance of Single Aircraft Turbojet Combustor at Simulated Idle, Cruise and Takeoff Conditions," *NASA TM-73780*, September 1977.
5. Blazowski, W.S. and Jackson, T.A., "Evaluation of Future Jet Fuel Combustion Characteristics," *AFAPL-TR-77-93*, July 1978.
6. Gleason, C.C., Oller, T.L., Shayeson, M.W., and Bahr, D.W., "Evaluation of Fuel Character Effects on J79 Engine Combustion System," *AFAPL-TR-79-2015*, General Electric Company, June 1979.
7. Gleason, C.C., Oller, T.L., Shayeson, M.W., and Bahr, D.W., "Evaluation of Fuel Character Effects on the F101 Engine Combustion System," *AFAPL-TR-79-2018*, General Electric Company, June 1979.
8. Vogel, R.E., Troth, D.L., and Verdouw, A.J., "Fuel Character Effects on Current, High Pressure Ratio, Can-Type Turbine Combustion Systems," *AFAPL-TR-79-2072*, General Motors Corporation, April 1980.
9. Moses, C.A. and Naegeli, D.W., "Fuel Property Effects on Combustor Performance," *MED 114*, Southwest Research Institute, March 1980.
10. Moses, C.A. and Naegeli, D.W., "Fuel Property Effects on Combustor Performance," *Gas Turbine Combustor Design Problems*, Lefebvre, A.H., ed. (Hemisphere Publishing Corp., 1980) pp. 39-69.
11. Gleason, C.C. and Bahr, D.W., "Fuel Property Effects on Life Characteristics of Aircraft Engine Combustors," *J. Energy* 4, 216-222 (1980).
12. Blazowski, W.S. and Maggiti, L., "Future Fuels in Gas Turbine Engines," *Alternative Hydrocarbon Fuels: Combustion and Chemical Kinetics*, Bowman, C.T. and Birkeland, J., eds. (American Institute of Aeronautics and Astronautics, New York, 1978) pp. 21-73.
13. Blazowski, W.S., "Future Jet Fuel Combustion Problems and Requirements," *Prog. Energy Combust. Sci.* 4, 177-199 (1978).
14. Szetela, E.J., Lohmann, R.P., and Smith, A.L., "Impact of Broad Specification Fuels on Aircraft Gas Turbine Combustors," *J. Energy* 4, 24-31 (1980).

15. Mellor, A.M. "Soot Studies in Gas Turbine Combustors and Other Turbulent Spray Flames," presented at General Motors Research Laboratories Symposium on Particulate Carbon, Formation during Combustion, October 1980 (to be published).
16. Blazowski, W.S., "Dependence of Soot Production on Fuel Blend Characteristics and Combustion Conditions," Gas Turbine Conference and Exhibit and Solar Energy Conference, March 1979. ASME Paper 79-GT-155.
17. Wyatt, W.R., Clark, J.A., Peters, J.E., and Mellor, A.M., "Size Distribution and Surface Area Measurements of Gas Turbine Combustor Smoke," *J. Energy* 3, 285-290 (1979).
18. Hoult, D.P. and Ekchian, A., "Soot Formation in a Turbulent Swirl Stabilized Laboratory Combustor," 25th International Gas Turbine Conference, March 1980. ASME Paper 80-GT-77.
19. Naegeli, D.W. and Moses, C.A., "Effect of Fuel Molecular Structure on Soot Formation in Gas Turbine Engines," 25th International Gas Turbine Conference, March 1980. ASME Paper 80-GT-62.
20. ASTM Method DI322-75, "Standard Method of Test for Smoke Point Aviation Turbine Fuels," Annual Book of ASTM Standards (American Society for Testing and Materials, Philadelphia, PA, 1975).
21. Van Treuren, K.W., "Sooting Characteristics of Liquid Pool Diffusion Flames," Master's Thesis, Princeton University, AFIT-CL-79-44T, July 1978.
22. Blazowski, W.S., Sarofim, A.F., and Keck, J.C., "The Interrelationship between Soot and Fuel NO_x Control in Gas Turbine Combustors," 25th International Gas Turbine Conference, March 1980. ASME Paper 80-GT-76.
23. Champagne, D.L., "Standard Measurement of Aircraft Gas Turbine Engine Exhaust Smoke," Gas Turbine Conference and Products Show, March 1971. ASME Paper 71-GT-88.
24. Minchin, S.T., "Luminous Stationary Flames: The Quantitive Relationship between Flame Dimensions at the Sooting Point and Chemical Composition, with Special Reference to Petroleum Hydrocarbons," *J. Inst. Petrol.* 17, 102-120 (1931).

APPENDIX A⁺

EFFECT OF MOLECULAR STRUCTURE ON INCIPIENT SOOT FORMATION

H.F. CALCOTE and D.M. MANOS*

AeroChem Research Laboratories, Inc.
P.O. Box 12, Princeton, New Jersey 08540

ABSTRACT

By defining a rational threshold soot index, TSI, varying from 0 to 100 to measure the onset of soot formation in both premixed and diffusion flames, it is shown that all of the data in the literature on premixed and diffusion flames, taken by many techniques, are consistent with respect to molecular structure for the two types of flames. There is a closer similarity between the effect of molecular structure on soot formation in premixed and diffusion flames than previously thought. The use of TSI permits one to use all of the literature data to interpret molecular structure effects and thus arrive at rules for predicting the effect of molecular structure for compounds which have not yet been measured or to convert the results from one experimental system to another. If a correlation can be demonstrated between the effect of molecular structure on soot formation in the laboratory and in practical systems, the TSI's will be important to the synfuels program in defining the desired fuels to be prepared from a given feed stock.

Prepared for submission to Combustion and Flame.

* Present address: Plasma Physics Laboratory, Princeton University, Princeton, N.J.

INTRODUCTION

As synfuels play a greater role in meeting future energy demands, a better understanding of the factors governing their propensity to form soot is required. Quantitative prediction of the soot forming characteristics of new fuels can best be achieved from an understanding of the quantitative behavior of their individual hydrocarbon constituents.

There are two distinct facets to the consideration of the effects of fuel molecular structure on sooting. First, as a given premixed fuel/oxidant combination is made fuel rich (or as the primary aeration of a diffusion flame is decreased), a rather sharp onset of sooting is observed. This facet of the tendency to soot is important in practical applications where the total absence of sooting is desirable. The second facet is that further increasing the fuel concentration beyond the point of soot onset causes increasingly greater quantities of soot to form at a rate which depends on fuel structure. In this paper we concentrate on the specification of the onset of soot formation. Data from a variety of measurements made in both premixed and diffusion flames have been gathered from the literature and correlated on this aspect of sooting. The objective was to determine the degree of consistency, or inconsistency, of the data in the literature on the effect of molecular structure on soot formation in both premixed and diffusion flames, and the relationship, if any, between the two types of flames. Assuming a consistency is established for the data, then the objective would be to deduce an empirical description of how molecular structure controls the onset of soot. Other people have considered the effect of molecular structure on soot formation but have limited themselves to data collected in a single type of apparatus where they have been limited by the number of compounds studied. These studies usually conclude that certain trends in the effect of molecular structure agree with results of previous

work, although significant differences in the actual numerical values occur between different studies. In this study we have made such comparisons quantitative so that separately obtained sets of data can be compared directly and so that all of the available data can be used to deduce molecular structure effects.

We define a "threshold soot index" (TSI) which ranks the fuels from 0 to 100, (0 = least sooty), independent of the particular experimental apparatus in which the data were obtained. A quantitative value for each molecule is thus obtained so that different molecules studied by different investigators (using different experimental apparatus) can be considered in elucidating the effect of molecular structure on soot formation. One of the first objectives will be to demonstrate the validity of the assumption of consistency underlying this statement.

This kind of information should be of great value in attempts to understand the relationship between laboratory data and engine data. Such correlations, if they could be demonstrated, would reduce the number of engine tests required to establish the effect of molecular structure on engine performance. The real impact should be on the synfuels engineer in determining the type of molecules to strive for in the refining processes. The situation is analogous to the empirical understanding of the relationship between octane or cetane number and molecular structure and the objectives of petroleum engineers in structuring the products of petroleum refineries.

SOURCES OF DATA

The data on incipient soot formation are divided into two categories: premixed flames and diffusion flames. Data on premixed flames were taken from Street and Thomas [1], Wright [2], Calcote and Miller [3], Grumer, Harris and Rowe [4], and Blazowski [5]. Data on diffusion flames came from the work of

Minchin [6], Clarke, Hunter, and Garner [7], Hunt [8], Schalla and McDonald [9], Van Treuren [10], and Schug, Manheimer-Timnat, Yaccarino, and Glassman [11].

In addition to measurements on pure hydrocarbons, some of these workers studied fuels consisting of mixtures of hydrocarbons and organic compounds containing heteroatoms (O, N, S, Cl, etc.). Only the reported data on unblended hydrocarbons, C_nH_m , are considered here.

The most extensive data set from premixed flames is that of Street and Thomas [1]. These authors used an apparatus in which a flow of fuel was mixed with air to form either a vapor mixture or fuel mist, according to the compound's vapor pressure. These mixtures were then burned in a shielded flame and the ratio of fuel/air was increased until a yellow tip was first observed. This critical composition was reported. Grumer et al. [4] burned only premixed fuel vapors, reporting fuel-air composition at the yellow-tip limit. Similar measurements on completely vaporized fuels were made by Calcote and Miller [3] with a shielded flame burner. They demonstrated a sensitivity of their results to the unburned mixture flow velocity, although at higher velocity their results were independent of velocity. Wright [2] used a heavily backmixed, jet-stirred combustor from which he reported the critical fuel/air ratio which caused the first visible appearance of soot on a probe filter placed in the reactor outlet. This reactor allowed richer mixtures to burn without sooting; a number of compounds found to soot in other premixed flame studies reached their rich blow-off limit without sooting in this apparatus. Additional studies from the same apparatus have been reported recently by Blazowski [5].

For diffusion flames Minchin [6] made measurements of the (now standard) smoke point employing a wick style burner in which the fuel flow was increased until soot was observed to be liberated from the tip of the flame. The flow

was decreased just enough to suppress the liberation of soot and the height of the flame, referred to as the "smoke point", was recorded. Hunt [8] performed the same type of measurement on a very large number of pure compounds, using a burner of different dimensions. Clarke and coworkers [7] also measured flame heights, as described above; however, they burned the liquids as pools in a funnel-shaped burner, rather than on wicks. By elevating the level of the liquid in such a funnel the area of the pool is increased and more fuel is vaporized into the flame. The physical characteristics of a duplicate of this burner were studied by Van Treuren [10] who reported excellent agreement with the values of Clarke et al. Van Treuren showed that the actual numerical results of such measurements depend strongly on the burner temperature and burner and chimney dimensions. Schalla and McDonald [9] used three different burners, one for gases and two for liquids. Liquids were burned either in a wick style lamp or in a burner with prevaporation. Rather than recording the flame height, Schalla and McDonald recorded the volume rate of fuel flow ($\text{cm}^3(\text{STP})\text{s}^{-1}$) at the point where further increases in fuel flow caused the onset of soot. Glassman and associates [11] used an apparatus similar to that described by Schalla and Hubbard [12] consisting of a 1 cm i.d. central fuel jet and a 10 cm concentric confining tube through which the flow of air was regulated. Both sooting heights and the critical flow velocity were measured.

Because of the various experimental differences between these studies, a direct comparison of the quantitative results is not possible without further processing the data. We will now show how the data were treated to condense all premixed flame data and all diffusion flame data into two internally consistent data sets.

DEFINITIONS AND METHOD OF TREATING DATA

In this section we define a threshold soot index, TSI, which is derivable from measured quantities of both premixed and diffusion flames. This allows one to consider all of the data available in these categories and to quantitatively compare TSI for different types of molecules. Qualitative comparisons of this sort, though common [13,14], can be grossly misleading.

It is generally recognized that substances with lower smoke points are in some sense "sootier" than those with higher smoke points. Minchin defined a parameter called "tendency to smoke" as a constant divided by the smoke point. This definition has been accepted since his 1931 paper. Similarly, it has been recognized that in premixed flames the lower the carbon to oxygen ratio, C/O, or the lower the critical equivalence ratio,¹ ϕ_c , the greater the tendency of the fuel to soot.

In defining TSI it is desirable to define a parameter which reflects the correlation of incipient sooting with molecular structure, i.e., the oxidative chemistry of the fuel, and does not reflect differences in transport properties due to the nature of the measurement apparatus or the quantity of oxygen which must diffuse into the flame front (in the case of diffusion flames).

For a premixed flame, consider two hypothetical hydrocarbon fuels of very different molecular weights or C/H ratios both of which liberate soot when burned in a premixed flame with a stoichiometric amount of oxidizer. It is clear that a definition of TSI as

$$TSI = a - b \phi_c \quad (1)$$

¹ ϕ_c is defined as the minimum equivalence ratio, ϕ , for sooting where $\phi = (\text{fuel flow}/\text{oxidizer flow})/(\text{fuel flow}/\text{oxidizer flow})_{\text{stoichiometric}}$.

with a and b constants for a given set of data will yield the same value for both of these hypothetical compounds. The use of C/O does not do this. We therefore adopt the definition of Eq. (1) in this work.

Minchin's definition of tendency to soot for diffusion flames as inversely proportional to the height of the flame which would just soot, contains an inherent flaw; it does not account for the increased height of the flame which would be required with increasing fuel molecular weights. An increase in molecular weight requires more oxygen to diffuse into the flame to consume a unit volume of the fuel. This can be accounted for by defining the threshold soot index for diffusion flames as:

$$TSI = a \left(\frac{MW}{h} \right) + b \quad (2)$$

where a and b are constants for any given experimental setup and h is the critical height of the flame for which soot is observed. A better approximation would be to employ the moles of air required for the combustion of one mole of fuel instead of M.W. The accuracy of the data and the arbitrariness of defining the products of combustion are such that the convenience of using the molecular weight is acceptable.

The critical volumetric flow velocity, V, is also used as a measure of the tendency to soot in diffusion flames. According to the Burke and Schuman theory of diffusion flames [15]

$$h = \frac{V}{4\pi C_f D} \quad (3)$$

where C_f is the concentration of fuel and D is an average diffusion coefficient of the system. This equation predicts a linear correlation between the height of a diffusion flame and the volumetric flow rate. This has been confirmed recently by Glassman and associates [11]. Thus we can also define

for a diffusion flame

$$TSI = a \left(\frac{MW}{V} \right) + b \quad (4)$$

where V is the critical volumetric flow rate for production of soot as used by Schallaa and McDonald.

To compare the various data sets we adjust the arbitrary proportionality constants, a and b , in Eqs. (1), (2), and (4) for each data set to minimize the error between the values of TSI for compounds which are common to more than one set of data. The resulting merged set of TSI values, spanning the range of hydrocarbons measured by all experimenters, is then linearly scaled so that the compounds have $0 \leq TSI \leq 100$. The calculation was done by picking the two compounds from the largest data set with the highest and the lowest MW/h (for diffusion flames) and solving Eq. (4) for a and b denoted as a_1 and b_1 . With these constants the TSI was calculated for each of the compounds in data set 1. For a second data set, two compounds were selected which were in common with the first data set and by assigning them the same TSI values as for the first data set, a_2^0 and b_2^0 of Eq. (4) were derived and used to calculate a TSI_2^0 value for each member of data set 2. Next a least-squares linear correlation of the two sets of data for TSI_1 and TSI_2^0 was made using the above derived constants for each set. This yielded m and C in the equation correlating the two sets of data

$$TSI_1 = m TSI_2^0 + C \quad (5)$$

The two sets of data can now be considered to have been merged so that $TSI_1 = TSI_2$. Thus the TSI for the second set of data on the same scale as data set 1 is calculated by substituting TSI_2^0 in the form of Eq. (4) in Eq. (5), yielding:

$$TSI_1 = TSI_2 = m a_2^0 \left(\frac{MW}{h} \right) + m b_2^0 + C \quad (6)$$

where $a_2 = m a_2^0$, $b_2 = m b_2^0 + C$ in Eq. (4) for data set 2. With the values of a_2 ,

and b_2 , the TSI values were calculated by Eq. (4) for all of the data in the second set. This process was repeated for each data set, yielding constants which minimize the differences between the various sets of data. For those compounds which occurred in more than one data set, the TSI's were averaged to give a mean value. Then to fix the TSI scale range from 0 to 100 the TSI of the lowest value in the total of all the data sets was set equal to 0 and the highest value equal to 100 [TSI (ethane) = 0, TSI (naphthalene) = 100]; the original values had deviated from these values in the averaging process.

This linear adjustment of the TSI_{0-100} was accomplished as follows:

$$TSI_{0-100} = (TSI - X) \left(\frac{100}{Y - X} \right) \quad (7)$$

where: TSI = TSI value being corrected

X = TSI of ethane on old scale

Y = TSI of naphthalene on old scale

The constants a and b reported in Table 1 are thus given by combining Eqs. (7) and (4).

$$TSI_{0-100} = \frac{100}{Y - X} \left(a_1 \left(\frac{MW}{h} \right) + b_1 - X \right) \quad (8)$$

or $a = \left(\frac{100}{Y - X} \right) a_1 \quad b = \frac{100}{Y - X} (b_1 - X)$

This process can clearly be iterated for any new data set, adjusting the total scale, or the new data set may be fit into the total data base by calculation of a and b for the new data through the least-squares linear correlation.

The data for premixed flames can be treated similarly.

The constants, a and b , for each data set are given in Table 1. These allow translation of the TSI for any fuel to the conditions of a particular experiment, even though that substance may not have been investigated under those conditions.

TABLE 1

Constants for Calculation of TSI from Original Data

Source	Original Data Form	a	b
<u>Premixed Flames</u>			
Street and Thomas [1]	ϕ_c	219	101
Grumer, Harris, and Rowe [4]	ϕ_c	181	81.6
Wright [2]	ϕ_c	204	78.1
Calcote and Miller [3]	ϕ_c	303	147
Blazowski [5]	ϕ_c	227	101
<u>Diffusion Flames</u>			
Minchen [6]	h	0.178	-15.7
Clarke, Hunter, and Garner [7]	h	0.381	-0.76
Hunt [8]	h	3.10	1.13
Schalla and McDonald [9]	v	0.322	0.85
Van Treuren [10]	h	0.594	-1.16
Schug, Manheimer-Timnat, Iaccarino, and Glassman [11]	v	0.144	-1.55

The consistency of the resulting data sets shown in Tables 2 and 3 may be judged by comparing the deviations in values for those compounds common to two or more data sets. In spite of the very different nature of premixed measurements and the uncertainties that are associated with each of them, it is clear from Table 2 that they are fairly consistent. When the data are averaged for these compounds the mean scatter introduced is less than $\pm 10\%$; only one data point in the total of 63 was excluded for reasons of gross disagreement. The above deviation is probably not more than the absolute error associated with the individual members of the set; some results are given to only one significant figure. Table 2 includes not only Bunsen burner type data but the data by Wright and Blazowski in a backmixed jet stirred reactor. The rationale for taking data in a jet stirred reactor was that the aerodynamics more closely duplicates that occurring in actual hardware, especially gas turbines. The correlation in Table 2 strongly indicates that chemistry, not aerodynamics, is controlling the critical composition for soot formation.

The mean scatter from averaging the diffusion flame data, Table 3, is less than $\pm 15\%$; if propane and propylene are excluded the mean scatter is less than $\pm 10\%$. Seven data points out of 146, or 5% of the data points were excluded. A data point was excluded only when three or more measurements were available for the same substance and one of them was obviously out of line--see the bracketed numbers in Table 3. Again the agreement between different investigators using different techniques emphasizes the importance of chemistry in determining the critical composition for soot formation.

TABLE 2
 Threshold Soot Index for Compounds Measured in Premixed Flames
 Data source indicated in brackets

Formula	Name	Mol. Wt.	C/H	Threshold Soot Index TSI
CH ₄	methane	16	0.250	34[4]
C ₂ H ₆	ethane	30	0.333	42[1] 28[4] 35 ± 7
C ₃ H ₈	propane	44	0.375	53[1] 47[3] 49[4] 50 ± 2
C ₄ H ₁₀	n-butane	58	0.400	61[1] 53[4] 57 ± 4
C ₅ H ₁₂	n-pentane	72	0.417	63[1]
C ₅ H ₁₂	isopentane	72	0.417	61[1]
C ₆ H ₁₄	n-hexane	86	0.429	65[1] 63[3] 64 ± 1
C ₆ H ₁₄	2-methyl pentane	86	0.429	65[1]
C ₆ H ₁₂	cyclohexane	84	0.500	58[1] 53[3] 56 ± 3
C ₈ H ₁₈	n-octane	114	0.444	72[1] 52[3] 62 ± 10
C ₈ H ₁₈	isooctane	114	0.444	65[1]
C ₁₀ H ₁₈	decalin ^a	138	0.556	85[1]
C ₁₂ H ₂₆	isododecane	170	0.462	70[1]
C ₁₆ H ₃₄	n-cetane	226	0.471	76[1]
C ₂ H ₄	ethylene	28	0.500	26[1] 33[3] 41[2] 24[5] 27[4] 30 ± 5
C ₃ H ₆	propylene	42	0.500	42[1] 37[2] {63[37]} ^b 40 ± 2
C ₄ H ₆	n-butene	56	0.500	53[1] 46[2] 50 ± 4
C ₄ H ₆	isobutene	56	0.500	62[2] 67[4] 64 ± 3
C ₅ H ₁₀	n-pentene	70	0.500	56[1]
C ₇ H ₁₄	n-heptene	98	0.500	5[1] 55[3] 60 ± 5
C ₄ H ₆	1,3-butadiene	54	0.667	77[2]
C ₂ H ₂	acetylene	26	1.00	-1.5[1] 1.6[3] 0.00 ± 1.5
C ₆ H ₆	benzene	78	1.00	68[1] 75[3] 93[2] 85[4] 80 ± 9
C ₇ H ₈	toluene	92	0.875	78[1] 93[3] 87[2] 86[5] 72[4] 83 ± 7
C ₈ H ₁₀	xlenes	106	0.800	85[1] 93[3] 90[2] 95[5] 91 ± 3
C ₉ H ₁₂	cumene ^c	120	0.750	83[1] 74[3] 79[2] 85[5] 80 ± 4
C ₁₀ H ₁₆	dicyclopentadiene ^d	130	1.00	85[2] 86[5] 86 ± 0
C ₁₀ H ₁₂	tetraline ^e	132	0.833	108[1] 92[2] 94[5] 98 ± 6

TABLE 2 (continued)

<u>Formula</u>	<u>Name</u>	<u>Mol. Wt.</u>	<u>C/H</u>	Threshold Soot Index TSI		
C ₁₁ H ₁₀	1-methyl naphthalene ^f	142	1.10	110[1]	86[2]	104[5] 100 ± 9

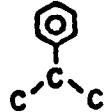
a



b

{ } Included in determining fit but excluded from average when plotting

c



d



e



f



TABLE 3

Threshold Soot Index for Compounds Measured in Diffusion Flames

Data source indicated in brackets

<u>Formula</u>	<u>Name</u>	<u>Mol. Wt.</u>	<u>C/H</u>	<u>Threshold Soot Index TSI</u>
C ₂ H ₆	ethane	30	0.333	1.2[9] -1.3[11] 0.0 ± 1.2
C ₃ H ₈	propane	44	0.375	1.3[9] -0.07[11] 0.7 ± 0.7
C ₃ H ₆	cyclopropane	42	0.500	3.2[9]
C ₄ H ₁₀	n-butane	58	0.400	1.6[9] 1.2[11] 1.4 ± 0.2
C ₄ H ₁₀	isobutane	58	0.400	2.2[9]
C ₅ H ₁₂	n-pentane	72	0.417	1.0[7] 1.3[8] 1.7[9] 1.3 ± 0.2
C ₅ H ₁₂	isopentane	72	0.417	1.6[7]
C ₅ H ₁₂	2,2-dimethyl propane	72	0.417	2.7[8] 3.8[9] 3.3 ± 0.5
C ₅ H ₁₀	cyclopentane	70	0.500	3.5[8] 3.0[7] 3.5[9] 3.3 ± 0.3
C ₆ H ₁₄	n-hexane	86	0.429	2.7[8] 2.3[9] 2.5 ± 0.2
C ₆ H ₁₄	2-methyl pentane	86	0.429	2.9[8] 2.9[10] 2.9 ± 0
C ₆ H ₁₄	3-methyl pentane	86	0.429	2.9[8] 2.6[9] 2.8 ± 0.1
C ₆ H ₁₄	2,2-dimethyl butane	86	0.429	3.3[8] 4.0[7] 3.6 ± 0.4
C ₆ H ₁₄	2,3-dimethyl butane	86	0.429	3.2[8]
C ₆ H ₁₂	methyl cyclopentane	84	0.500	5.0[8] 4.8[9] 4.9 ± 0.1
C ₆ H ₁₂	cyclohexane	84	0.500	3.2[8] 3.4[7] 3.0[9] 3.2 ± 0.1
C ₇ H ₁₆	n-heptane	100	0.438	3.0[8] 2.5[10] 2.6[9] 2.7 ± 0.2
C ₇ H ₁₆	2-methyl hexane	100	0.438	3.2[8]
C ₇ H ₁₆	3-methyl hexane	100	0.438	3.2[8]
C ₇ H ₁₆	2,3-dimethyl pentane	100	0.438	3.5[8]
C ₇ H ₁₆	2,4-dimethyl pentane	100	0.438	3.6[8]
C ₇ H ₁₄	methyl cyclohexane	98	0.500	4.2[8] 4.6[7] 4.4 ± 0.2
C ₈ H ₁₆	n-octane	114	0.444	3.3[8] 3.2[10] 3.2[9] 3.2 ± 0.1
C ₈ H ₁₆	2-methyl heptane	114	0.444	3.5[8]
C ₈ H ₁₆	3-methyl heptane	114	0.444	3.7[8]
C ₈ H ₁₆	4-methyl heptane	114	0.444	4.0[8]
C ₈ H ₁₆	3-ethyl hexane	114	0.444	4.0[8]
C ₈ H ₁₆	2,2-dimethyl hexane	114	0.444	4.5[8]
C ₈ H ₁₆	2,3-dimethyl hexane	114	0.444	3.8[8]
C ₈ H ₁₆	2,2,4-trimethyl pentane	114	0.444	5.0[8] 6.1[7] 5.6 ± 0.5
C ₈ H ₁₆	2,3,4-trimethyl pentane	114	0.444	5.7[7]

TABLE 3 (continued)

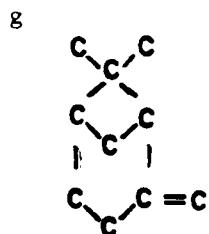
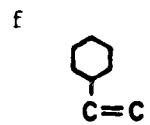
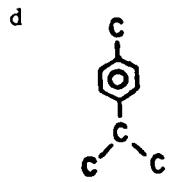
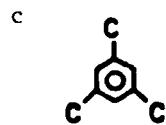
Formula	Name	Mol. Wt.	C/H	Threshold Soot Index TSI
C ₆ H ₁₆	2,3,3-trimethyl pentane	114	0.444	5.7[7]
C ₆ H ₁₆	2-methyl 3-ethyl pentane	114	0.444	4.4[8]
C ₆ H ₁₆	1,3-dimethyl cyclohexane	112	0.500	5.9[8]
C ₆ H ₁₆	ethyl cyclohexane	112	0.500	4.6[8]
C ₉ H ₂₀	nonane	128	0.450	4.1[9]
C ₉ H ₂₀	isononane	128	0.450	5.0[9]
C ₁₀ H ₂₂	decane	142	0.485	4.1[8] 4.5[10] 4.3 ± 0.2
C ₁₀ H ₁₈	decalin	138	0.556	12[8] 13[7] {3.7[6]} ^a 13 ± 0.5
C ₁₁ H ₂₄	undecane	156	0.458	4.3[8]
C ₁₂ H ₂₆	dodecane	170	0.466	4.8[8]
C ₁₃ H ₂₈	tridecane	184	0.464	5.2[8]
C ₁₄ H ₃₀	tetradecane	198	0.467	5.4[8]
C ₂ H ₄	ethylene	28	0.500	1.3[9] 1.3[11] 1.3 ± 0
C ₃ H ₆	propylene	42	0.500	2.6[9] 6.9[11] 4.7 ± 3.8
C ₄ H ₈	n-butene	56	0.500	4.4[9]
C ₄ H ₈	2-butene	56	0.500	4.3[9]
C ₄ H ₈	isobutene	56	0.500	4.8[9]
C ₅ H ₁₀	1-pentene	70	0.500	4.8[7] 3.5[9] 4.2 ± 0.6
C ₅ H ₈	cyclopentene	68	0.625	15[9]
C ₆ H ₁₂	hexene	84	0.500	3.9[8] 4.9[7] {8.1[10]} 4.4[9] 4.4 ± 0.3
C ₆ H ₁₀	cyclohexene	82	0.600	6.3[8] 5.8[7] 5.0[9] 5.7 ± 0.5
C ₇ H ₁₄	1-heptene	98	0.500	4.1[8] 4.5[7] 5.1[9] 4.6 ± 0.4
C ₇ H ₁₄	2-heptene	98	0.500	4.3[8] 5.3[9] 4.8 ± 0.5
C ₈ H ₁₆	1-octene	112	0.500	4.4[8]
C ₈ H ₁₆	2-octene	112	0.500	4.4[8]
C ₁₀ H ₂₀	decene	140	0.570	5.5[8] 6.2[7] 7.6[9] 6.5 ± 0.8
C ₁₂ H ₂₄	dodecene	168	0.500	6.4[8]
C ₁₂ H ₂₂	dicyclohexyl ^b	166	0.545	10[8] 11[7] 10 ± 0.2
C ₁₄ H ₂₈	tetradecene	196	0.500	7.6[8]
C ₁₆ H ₃₂	hexadecene	224	0.500	8.3[8]
C ₁₈ H ₃₆	octadecene	252	0.500	9.2[8]
C ₂ H ₂	acetylene	26	1.00	2.7[9] 4.6[11] 3.9 ± 0.7
C ₃ H ₄	propyne	40	0.750	5.9[9]

TABLE 3 (continued)

Formula	Name	Mol. Wt.	C/H	Threshold Soot Index TSI
C ₅ H ₈	pentyne	68	0.625	15[9]
C ₆ H ₁₀	hexyne	82	0.600	20[9]
C ₄ H ₆	1,3-butadiene	54	0.667	26[9] 24[11] 25 ± 0.9
C ₈ H ₁₄	2,5-dimethyl,1,5-hexadiene	110	0.570	34[9]
C ₆ H ₆	benzene	78	1.00	31[8] 30[7] {24[9]} 31 ± 0.4
C ₇ H ₈	toluene	92	0.875	48[8] {34[7]} 52[6] 48[10] 50[9]
C ₈ H ₁₀	xylene	106	0.800	63[8] 44[7] 46[10] 51 ± 8
C ₈ H ₁₀	ethyl benzene	106	0.800	56[8] 61[6] {75[9]} 58 ± 3
C ₉ H ₁₂	mesitylene ^c	120	0.750	47[8]
C ₉ H ₁₂	trimethylbenzenes	120	0.750	47[8]
C ₉ H ₁₂	cumene	120	0.750	63[8]
C ₉ H ₁₂	propyl benzene	120	0.750	47[8] {111[9]}
C ₁₀ H ₁₄	p-cymene ^d	134	0.714	84[8] 39[7] 61 ± 23
C ₁₀ H ₁₄	butyl benzene	134	0.714	70[8]
C ₁₀ H ₁₄	sec butyl benzene	134	0.714	60[8]
C ₁₀ H ₁₄	tert butyl benzene	134	0.714	84[8]
C ₁₀ H ₁₄	diethyl benzene	134	0.714	60[8]
C ₁₁ H ₁₆	sec pentyl benzene	148	0.688	58[8]
C ₁₁ H ₁₆	tert pentyl benzene	148	0.688	58[8]
C ₁₂ H ₁₈	m-di-isopropyl benzene	162	0.667	51[7]
C ₁₂ H ₁₆	phenyl cyclohexane	160	0.750	72[8]
C ₁₀ H ₁₂	tetralin	132	0.833	69[8] 41[7] 58[6] 56 ± 10
C ₉ H ₈	indene ^e	116	1.125	52[8]
C ₆ H ₈	styrene ^f	104	1.000	81[8]
C ₁₀ H ₁₆	pinene ^g	136	0.625	24[7]
C ₁₀ H ₈	naphthalene	128	1.25	100[8]
C ₁₁ H ₁₀	1-methyl naphthalene	142	1.10	89[8] 89[6] 89 ± 0
C ₁₁ H ₁₀	2-methyl naphthalene	142	1.10	89[8]
C ₁₂ H ₁₂	dimethyl naphthalenes	156	1.00	98[8]

TABLE 3 (continued)

^a { } Included in determining fit but excluded from average.



RESULTS AND DISCUSSION

It was demonstrated in the previous section that measurements of the threshold for soot formation for either premixed or diffusion flames made by many different investigators using different methods are consistent when the sets of data are appropriately treated using two constants to normalize each data set. This implies that chemistry is the controlling process in soot formation in both premixed and diffusion flames.

Before discussing the question of a correlation between the premixed data and the diffusion data, the effect of molecular structures on premixed and diffusion flames will be discussed separately.

Premixed Flames

Most of the TSI data in Table 2 are plotted against the number of carbon atoms in the molecule in Fig. 1. To simplify the figure, smooth curves have been drawn through the n-alkane and n-alkene data. Isomers have been left off because inspection of Table 2 shows that they generally produce only a slightly higher TSI. The most striking feature of Fig. 1 is that most of the data fall roughly in a band, with TSI increasing with number of carbon atoms; the slope is about 7 TSI units per carbon atom. Exceptions are acetylene, 1,3-butadiene, and the higher molecular weight alkanes and alkenes. When TSI is plotted against the C/H ratio, Fig. 2, butadiene is no longer out of order. It is also interesting that butadiene (as does acetylene) attains its maximum burning velocity [16] and minimum ignition energy [17] in very rich mixtures compared to other hydrocarbons. For example, butadiene has a maximum burning velocity of 57 cm s^{-1} at $\phi = 1.23$ while butene has a maximum burning velocity of 45 cm s^{-1} at $\phi = 1.08$. Most hydrocarbons reach their maximum burning velocity between $\phi = 1.0$ and 1.1.

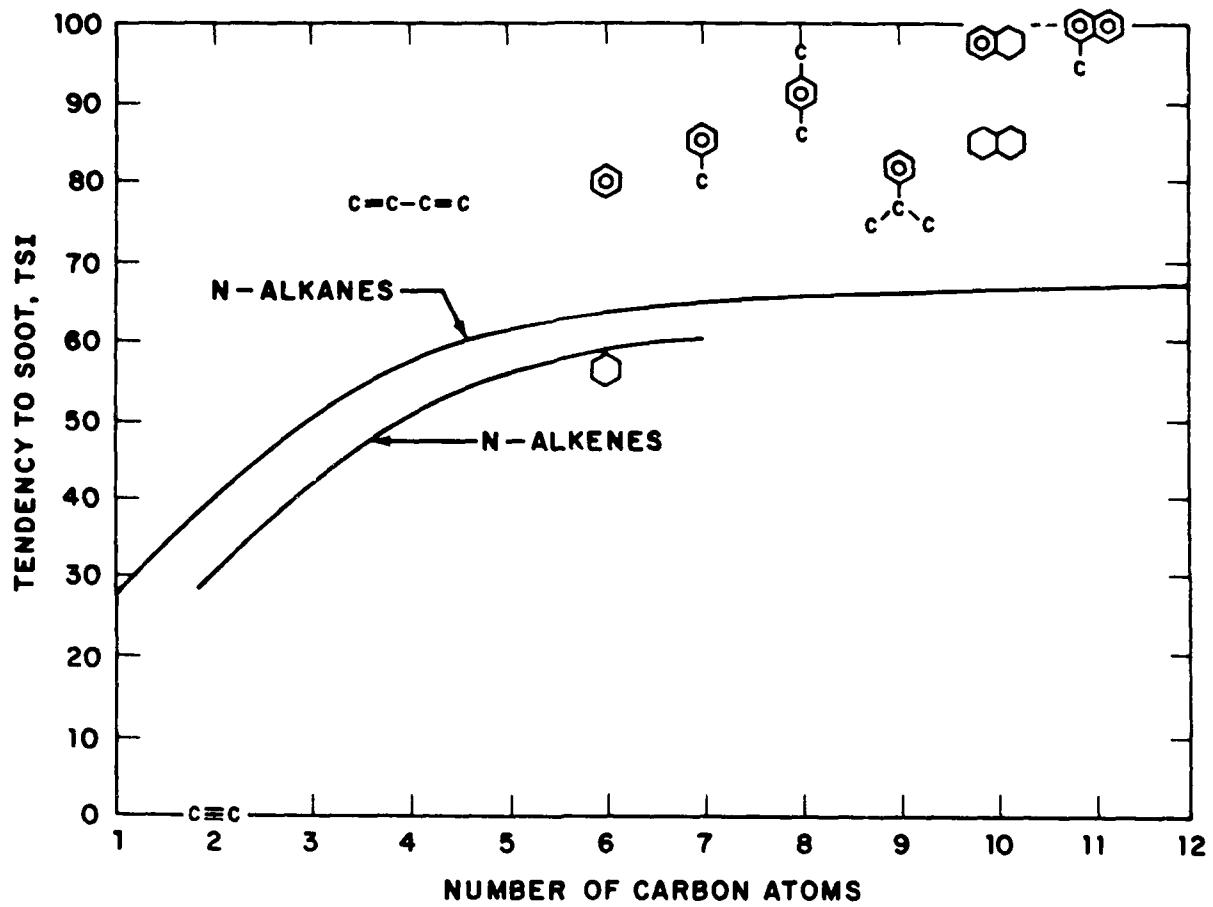


Figure 1. Effect of Molecular Structure on Soot Formation
In Premixed Flames

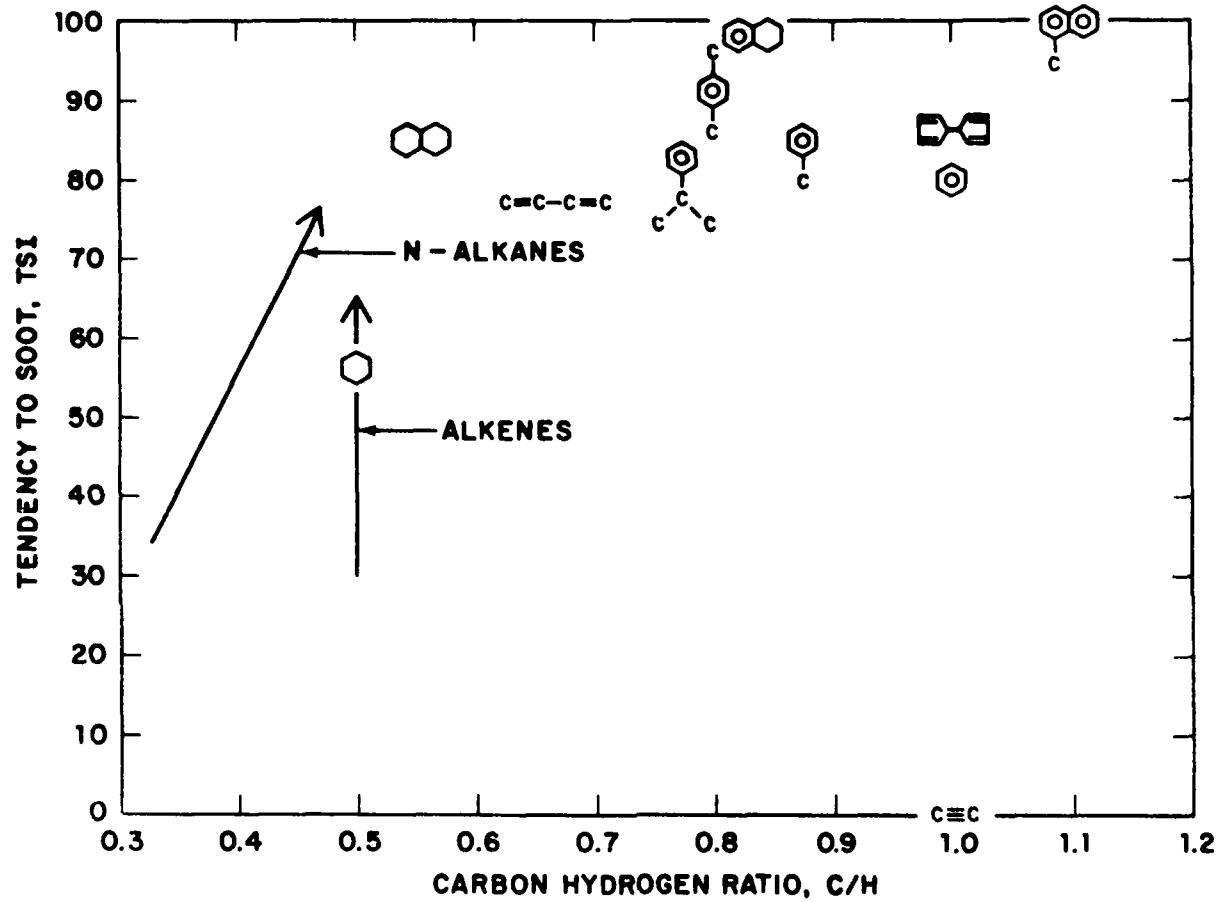


Figure 2. Effect of Molecular Structure on Soot Formation
In Premixed Flames

Arrows indicate increasing molecular weight.

The adiabatic flame temperature of acetylene is considerably greater than that of the other species; this may tend to mask the effect of molecular structure. It is clear, however, that the temperature is not the controlling factor in the tendency of a fuel to soot (cf. Refs. 18 and 19); for Bunsen burner flames the calculated adiabatic flame temperatures at the incipient soot point for acetylene, benzene, and n-hexane are 2380, 2200, and 1850 K, respectively, which bears very little relationship to their position on Fig. 1. Blazowski reports measured temperatures in a stirred reactor at the incipient soot limit for ethylene, 1-methyl naphthalene, and toluene of 1550, 1905, and 1951 K, respectively, which again bears little relationship to their position in Fig. 1.

It is also clear from Fig. 1 that increasing aromatic character increases the tendency to soot; compare, e.g., cyclohexane to benzene (TSI = 56 to 80), and decalin to tetralin (TSI = 85 to 98).

Based only on their results, Street and Thomas [1] reported the following (frequently quoted [13,14]) qualitative, relative ordering for the tendency to soot of hydrocarbons in premixed flames:

acetylene < alkenes < iso-alkanes < α -alkanes < monocyclic aromatic hydrocarbons < naphthalenes

As shown in Fig. 1 these are rather poor summaries of the actual situation. Consideration of the quantitative ordering demonstrates that the reported trend is misleading. Further, it is clear that the effect of increasing the number of carbons within a family is sometimes much greater than changing families at fixed carbon number. As an illustration, consider the relatively small differences between hexane (TSI = 64) and hexene (TSI = 58 interpolated) compared to changing from ethylene (TSI = 30) to heptene (TSI = 60), or ethane (TSI = 35) to pentane (TSI = 63).

Another frequently reported qualitative trend is the increase in tendency to soot with increasing C/H ratio [20,21]. The results in Table 2 plotted in Fig. 2 against C/H ratio, show that while there is a general increase in tendency to soot with increasing C/H ratio, the trend is weak and thus of limited predictive value. All of the alkenes at fixed C/H should be equal but have TSI values from 30 to 65, and acetylene with one of the highest C/H ratios has (TSI = 0) the lowest value of any compound measured; further, acetylene and benzene have the same C/H but TSI = 0 and 80, respectively.

Street and Thomas suggested that the somewhat higher TSI of aromatics in premixed flames may be caused by the ability of the benzene ring to resist oxidation and survive into the burnt gas zone. Fenimore, Jones, and Moore [22] subsequently studied the onset of soot in premixed flames as a function of various species concentrations in the burnt gas zone. They found that the correlation between sooting and the survival of benzene into this zone was quite strong. In a recent review summarizing the role of aromatics in soot formation, Bittner and Howard [23] confirm this observation, but suggest that more information on the role of intact aromatics will be required to clarify the reasons for this large apparent enhancement.

Clearly more data are required on the effect of molecular structure on soot formation in premixed flames and that data should include the effect of temperature.

Diffusion Flames

Much of the data in Table 3 have been plotted in Figs. 3 and 4. Smooth curves have been drawn through the n-alkanes, n-alkenes, and n-alkynes. Isomers and cyclic structures for these substances have been deleted because they differ little from the normal compound and the tendency to soot of the alkanes and alkenes is small compared to other structures. The effect of

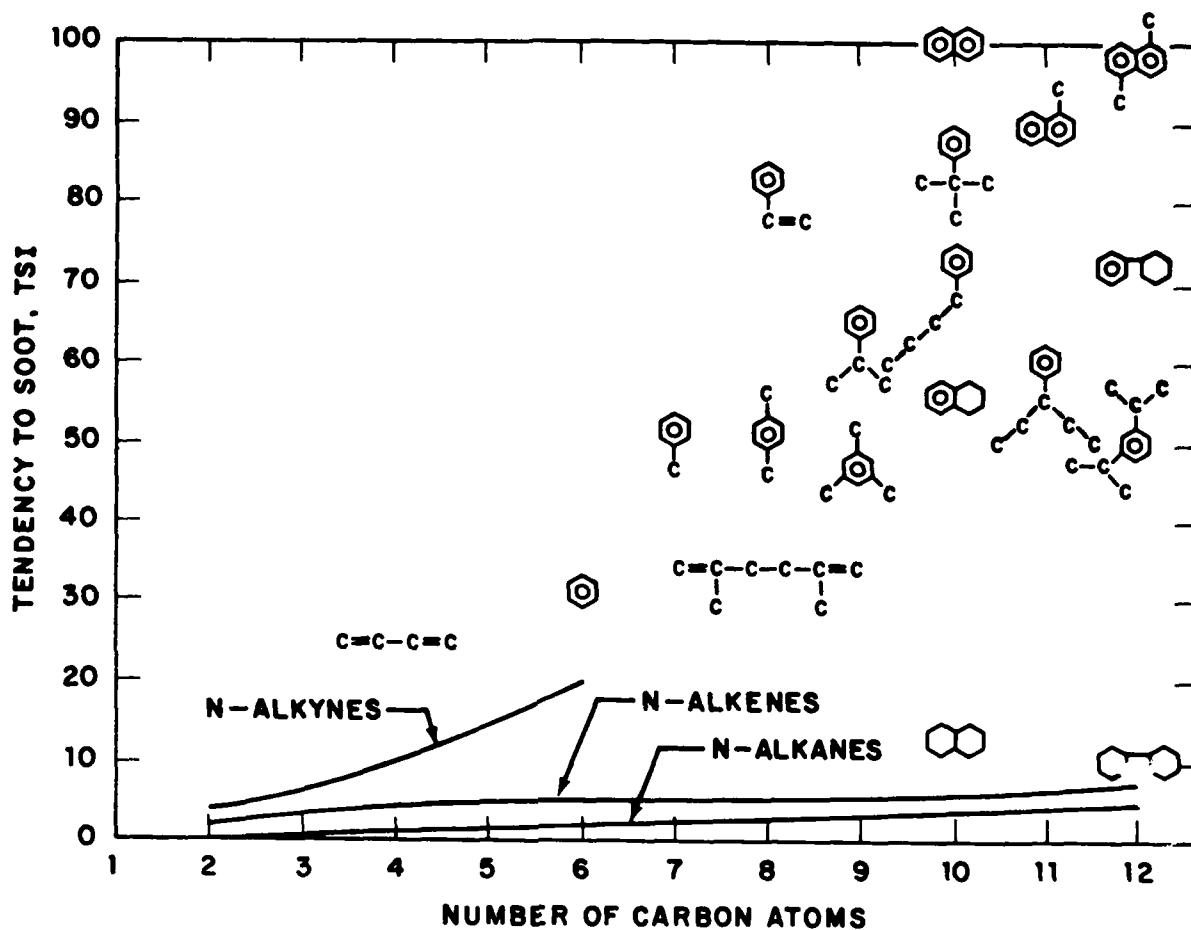


Figure 3. Effect of Molecular Structure on Tendency to Soot in Diffusion Flames

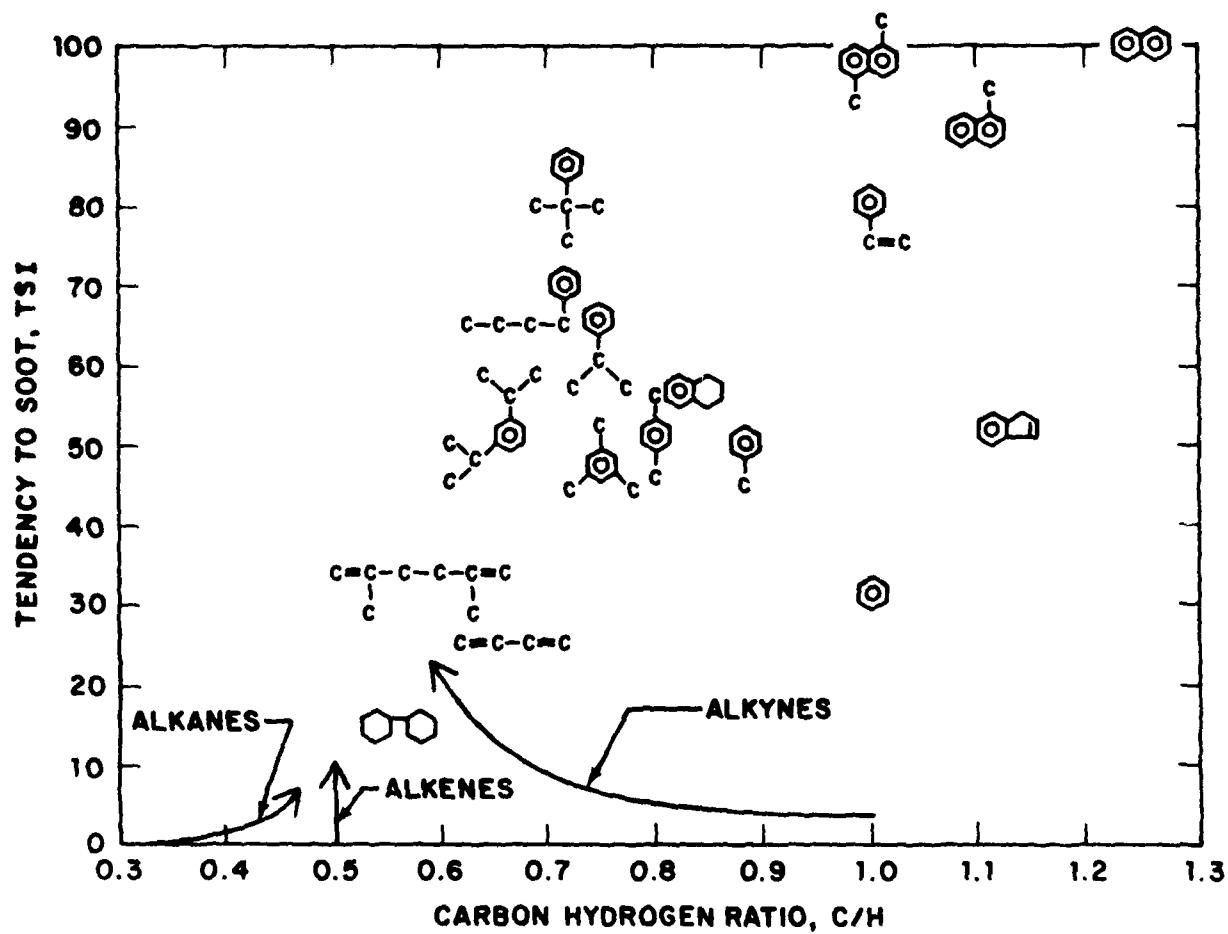


Figure 4. Effect of Molecular Structure on Tendency to Soot in Diffusion Flames

Arrows indicate increasing molecular weight.

isomeric structure is demonstrated by examining the octanes in Table 3. This table demonstrates what Clarke et al. [7] recognized, that the more compact the molecular structure the greater the tendency to soot.

The most striking feature of Fig. 3 is that most of the data, with the exception of the alkanes and alkenes, but including the alkynes, fall in a band with TSI increasing with number of carbon atoms, with slope varying from about 6 to 12 per carbon atom. This is better demonstrated when all of the data in Table 3 except that for the alkanes and alkenes, are plotted on a single graph. Only typical molecules are plotted in Fig. 3 because the displayed structures would overlap; the molecules with greatest deviation from the rest of the data have been included however. Butadiene again stands out as having a greater tendency to soot than any other small molecule; unfortunately, there are no other examples of conjugated systems. Glassman [11,19] interprets this observation as indicating that butadiene may be a major "precursor element in soot nucleation". Again, however, when TSI is plotted against C/H, Fig. 4, butadiene falls in with all the other fuels. Styrene with its conjugated double bond is also an outstanding sooter in Fig. 3 but falls within the other fuels in Fig. 4 when TSI is plotted against C/H.

The second most notable feature of Fig. 3 is the very low tendency of the alkanes and alkenes to soot and the major importance of aromatic character on the tendency to soot.

The failure of C/H to correlate the data is vividly clear in Fig. 4 in the comparison of acetylene and benzene, both having C/H = 1.0 but TSI of 3.9 and 31, respectively, or the trend from acetylene to hexyne with C/H from 1.0 to 0.6 and TSI from 3.9 to 20. We note that it has erroneously been reported [24] that the incipient sooting tendency decreases with increasing size for all compounds except paraffins. These conclusions were based on Fig. 6 of

Minchin [6] which has been interpreted as summarizing his experimental data. In fact the credit for this data is usually given to Clarke, Hunter, and Garner [7] who simply redrew Minchin's curves. Minchin's Fig. 6 is actually the result of a hypothetical calculation based on only a few data points. The relationship used in that calculation is not in agreement with the extensive data subsequently collected by other workers.

It is sometimes stated that in diffusion flames soot formation increases in the order [14]

pa affins < mono-olefins < di-olefins < acetylenes < benzenes < naphthalenes

Reference to Fig. 3 demonstrates how misleading this qualitative statement is when compared with quantitative data.

Comparison between Premixed and Diffusion Flames

It is classical mythology to recognize the different tendency to soot of premixed and diffusion flames [13,14]. Comparison of Figs. 1 and 3 show some differences and much in common. The most striking difference is the relative position of the alkenes and alkanes on the two figures; this is determined by the relative position of acetylene with respect to these two groups of compounds. In premixed flames acetylene has a much lower tendency to soot than the alkanes and alkenes but in diffusion flames it has a greater tendency to soot. In addition, the tendency to soot for the alkanes and alkenes is reversed in the two flames. Nevertheless, the tendency to soot increases with increasing molecular weight (increasing number of carbon atoms) in both flames for both classes of compounds, and the tendency to soot increases with isomerization (increasing molecular compactness) in both flames--see Tables 2 and 3. Both Figs. 1 and 3 show major overall trends in common when the total range of fuels is considered. At the extremes in both flames are acetylene

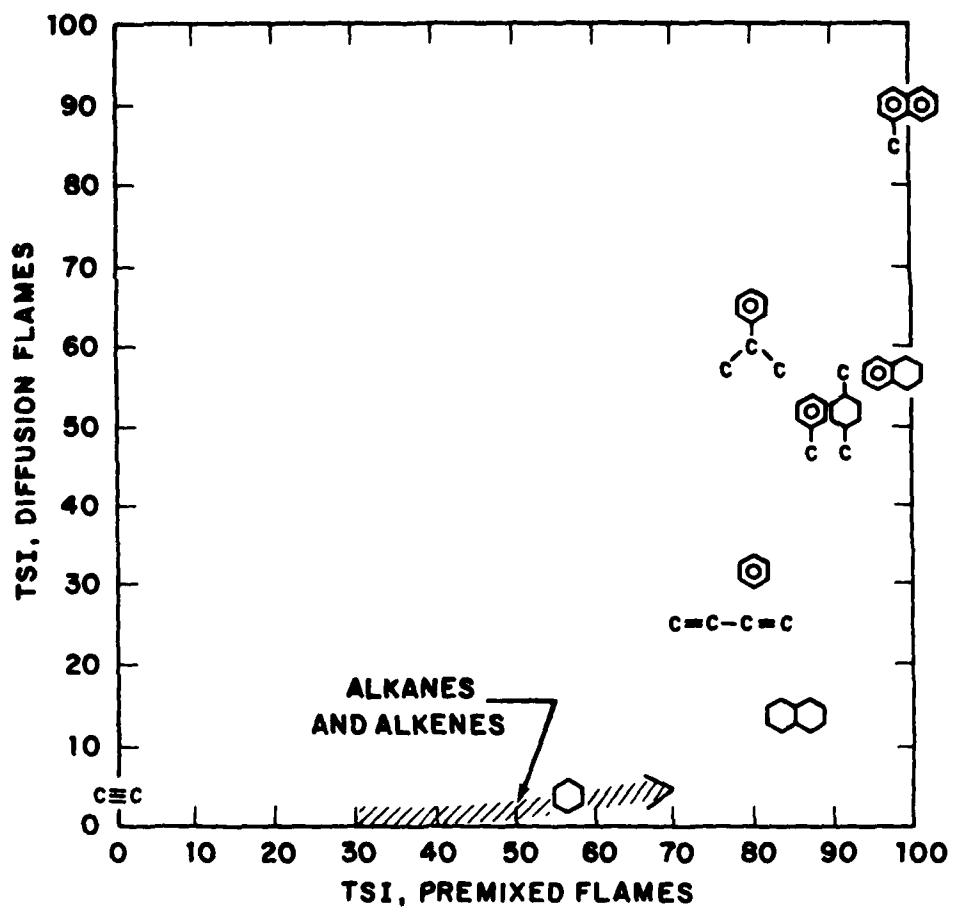


Figure 5. Comparison of Diffusion And Premixed Flames

and the naphthalenes. Further, it is apparent that aromatic character plays a dominant role in both flame types and 1,3-butadiene has a greater tendency to soot in both flames than the corresponding alkane or alkene when TSI is plotted against numbers of carbon atoms but not when plotted against C/H.

The fuels in common between the two flames are compared in Fig. 5. All of the alkanes and alkenes fall in the cross-hatched area. The correlation, although not linear, between the premixed and diffusion flames is surprisingly good. In diffusion flames differences between molecular structure of alkanes and alkenes cause only a small change in TSI while in premixed flames the change is more dramatic; on the other hand, for mono- and di-cyclic compounds large changes are noted for diffusion flames and small changes for premixed flames. It is obvious that more data on premixed flames are required; these are being collected in our laboratory.

The choice of definitions for TSI was somewhat arbitrary; a different choice should be possible to force the points in Fig. 5 to fall more nearly on a 45° line. It should also be pointed out that the manner of presentation of the data as TSI for the whole range of fuels appears to suppress the differences, especially in diffusion flames, between the alkanes, alkenes, and alkynes, although on a percentage basis the differences between these may be quite large. Another caveat is in order--the data reported here should not be interpreted as applying to practical systems such as turbojets, diesels, or power plants until a correlation between the laboratory system and the practical system has been demonstrated. The early examination of such correlations is of great importance to the synfuels program.

SUMMARY

By defining a rational threshold soot index, TSI, varying from 0 to 100 to measure the onset of soot formation in premixed and diffusion flames, it is shown that all of the data in the literature on premixed and diffusion flames, taken by many techniques, can be successfully correlated with respect to molecular structure. The differences in effect of molecular structure between premixed and diffusion flames are less than previously thought. The major differences between premixed and diffusion flames are the relative order of alkanes, alkenes, and alkynes; the relative importance of aromatic structure, isomerization, or increasing molecular size is the same. The role of C/H, often taken as important in determining the effect of molecular structure, is of very little value in correlating data from laboratory systems.

For premixed flames, the effect of molecular structure on the onset of soot formation as measured by the TSI can be tentatively summarized, until more data are available, in approximately decreasing order of importance:

1. TSI is strongly influenced by the number of carbon atoms in the molecule, about 7 TSI per carbon atom. Two exceptions to the rule are acetylene with a TSI of 0, about 30 TSI below any other molecule, and butadiene, 20 TSI greater than n-butane.
2. Aromatic character increases the tendency to soot. TSI is increased 15 to 25 units on converting a saturated ring to an aromatic ring. (The change from tetralin to methyl naphthalene is, however, very small.)
3. n-alkanes and iso-alkanes have essentially the same TSI (iso-alkanes slightly higher) starting at 35, rising to about 65 at pentane and then rising more slowly for larger molecules.

4. Alkenes fall below alkanes by about 10 TSI units for small molecules, decreasing to about 5 TSI units for larger molecules.

5. Adding a side chain to an aromatic molecule increases the TSI; lengthening the side chain decreases the TSI.

For diffusion flames the effect of molecular structure on the onset of soot formation can be summarized, in approximately decreasing order of importance:

1. TSI, with the exception of alkanes, and alkenes, but including the alkynes, is strongly influenced by the number of carbon atoms in the molecule, 6 to 12 TSI per carbon atom. Two major exceptions to the rule are 1,3-butadiene and styrene which are about 15 and 20 TSI, respectively, above the average curve.
2. Aromatic character greatly increases the tendency to soot; TSI is increased for changing a saturated ring to an aromatic ring by from 25 to 60.
3. Alkanes and alkenes have very low tendencies to soot, TSI < 7, with alkenes having TSI from 2 to 6 above alkanes.
4. Isomeric or cyclic structures for alkanes or alkenes do not compare in increasing the tendency to soot with increasing aromatic character; however, making an alkene or alkane more compact generally increases the tendency to soot by as much as 80%.
5. Multi-ring structures including saturated rings increase the tendency to soot.
6. The addition of a side chain to an aromatic molecule has complex effects, generally increasing TSI but for long side chains decreasing TSI.

ACKNOWLEDGMENT

This research was sponsored by the Air Force Office of Scientific Research (AFSC), United States Air Force under Contract F49620-77-C-0029. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. The authors also gratefully acknowledge the helpful discussions during this work with Drs. R.K. Gould and D.B. Olson.

REFERENCES

- [1] Street, J.C. and Thomas, A., Fuel 34: 4 (1955).
- [2] Wright, F.J., Twelfth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1969, p. 867.
- [3] Calcote, H.F. and Miller, W.J., "Ionic Mechanisms of Carbon Formation in Flames," TP-371, AeroChem Research Laboratories, Inc. (May 1978); Fall Technical Meeting, Eastern Section; The Combustion Institute, 10-11 November 1977.
- [4] Grumer, J., Harris, M.E., and Rowe, V.R., "Fundamental Flashback, Blow-off, and Yello-tip Limits of Fuel Gas-air Mixtures," Bureau of Mines, Rep. of Investigations 5225 (1956).
- [5] Blazowski, W.S., Combust. Sci. Technol. 21: 87 (1980).
- [6] Minchin, S.T., J. Inst. Petrol. 17: 102 (1931).
- [7] Clarke, A.E., Hunter, T.G., and Garner, F.H., J. Inst. Petrol. 32:627 (1946).
- [8] Hunt, R.A. Ind. Eng. Chem. 45: 602 (1953).
- [9] Schalla, R.L. and McDonald, G.E., Ind. Eng. Chem. 45: 1497 (1953)
- [10] Van Treuren, K.S., "Sooting Characteristics of Liquid Pool Diffusion Flames," M.S. Thesis, Princeton Univ., Dept. Mech and Aero. Eng. (July 1978).
- [11] Schug, K.P., Manheimer-Timnat, Y., Yaccarino, P., and Glassman, I., Combust. Sci. Technol. 22: 235 (1980).
- [12] Schalla, R.L. and Hubbard, R.R., "Formation and Combustion of Smoke in Flames, in Basic Consideration of Hydrocarbon Combustion," NACA Report 1300, Chap. IX (1959).
- [13] Gaydon, A.G. and Wolfhard, H.G., Flames. Their Structure, Radiation and Temperature, Chapman and Hall, London, 4th ed., 1978, Chap. VIII.

- [14] Glassman, I., Combustion, Academic Press, New York, 1973, p. 246.
- [15] Lewis, B. and Von Elbe, G., Combustion, Flames and Explosions of Gases, Academic Press, New York, 2nd ed., 1961, p. 479.
- [16] Gibbs, G.J. and Calcote, H.F., J. Chem. Eng. Data 4: 226 (1959).
- [17] Calcote, H.F., Gregory, C.A., Jr., Barnett, C.M., and Gilmer, R.B. Ind. Eng. Chem. 44: 2656 (1952).
- [18] Glassman, I. and Yaccarino, P., "The Temperature Effect in Sooting Diffusion Flames," to be published in proceedings of The Eighteenth Symposium (International) on Combustion.
- [19] Glassman, I., "Phenomenological Models of Soot Processes in Combustion Systems," Princeton Univ. Dept. Mech. and Aero. Eng. Report 1450, AFOSR TR 79-1147 (July 1979).
- [20] Longwell, J.P., in Alternative Hydrocarbon Fuels: Combustion and Chemical Kinetics (C.T. Bowman and J. Birkeland, Eds.) Progress in Astronautics and Aeronautics, AIAA, New York, 1978, Vol. 62, p. 3.
- [21] Blazowski, W.S. and Maggitti, L., ibid., p. 21.
- [22] Fenimore, C.P., Jones, G.W., and Moore, G.E., Sixth Symposium (International) on Combustion, Butterworths, London, 1956, p. 140.
- [23] Bittner, J.D. and Howard, J.B., in Alternative Hydrocarbon Fuels: Combustion and Chemical Kinetics (C.T. Bowman and J. Birkeland, Eds.) Progress in Astronautics and Aeronautics, AIAA, New York, 1978, Vol. 62, p. 335.
- [24] See e.g., Fig. 4 of Ref. 7; Fig. 10 of Ref. 14; Fig. 8.1 of Ref. 13; or Fig. 5.1 of Palmer, H.B. and Cullis, C.F., in Chemistry and Physics of Carbon (P.L. Walker, Jr., Ed.) Marcel Dekker, Inc., New York, 1965.

INITIAL DISTRIBUTION

OASD(I&L)EES	1
OUSDR&E	1
OSAF/MIQ	1
DTIC/DDA-2	2
OSAF/PAM	1
HQ USAF/LEEVVP	1
AEDC/DOTR	1
AFOSR/NA	1
AUL/LSE 71-249	1
USAFA/Library/DESEL	1
Ch, Environmental Chem Div, USAEHA	1
Cmdr, USA Med Bioengrg R&D Lab	1
AFATL/DLODL	1
NAPC/Code PE71:AFK	1
FAA/AEQ-10	1
Library, Chemical Abstract Service	1
HQ AFESC/TST	1
HQ AFESC/RDV3	10
AFWAL/TSG	1
AFWAL/POSF	1
AFWAL/POTC	1
AFATL/DLODR	1

